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Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC

Task 4
Test Development Review

ORIGINAL

Prepared by T. M. Ahn, K. S. Czyscinski, E. M. Franz, C. J. Klamut, B. S. Lee, N. S. McIntyre, K. J. Swyler, R. J. Wilke

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Prepared for
U.S. Nuclear Regulatory Commission

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IMPORTANT NOTICE

All references made to the BNL interim reports, "NRC Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria," Tasks 1-5, should be disregarded. The following references should be inserted in their places, as applicable.

R. Dayal, et al., "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 1: Waste Package Overview," NUREG/CR-2333, Vol. 1, BNL-NUREG-51458, February 1982.

G. Bida, et al., "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 2: Alternative TRU Technologies," NUREG/CR-2333, Vol. 2, BNL-NUREG-51458, February 1982.

D. Majumdar, et al., "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 3: Waste Inventory Review," NUREG/CR-2333, Vol. 3, BNL-NUREG-51458, February 1982.

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M.S. Davis, "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 5: National Waste Package Program," NUREG/CR-2333, Vol. 5, BNL-NUREG-51458, February 1982.

ABSTRACT

This final report describes the development of testing methods by the Department of Energy for a high level nuclear waste package. Such methods serve several purposes: quality control of the materials being used, comparative testing of alternative components, and eventual qualification of the waste package to comply with Nuclear Regulatory Commission criteria in 10 CFR 60. Since the issuance of the earlier Interim Report, a major effort has been spent reviewing the activities of the Materials Characterization Organization. To date this organization is dealing successfully with comparative testing aspects of the waste package, but compliance testing, in general, still remains to be addressed. Testing and characterization of each component are discussed in separate chapters. Testing of the waste form is considered in terms of chemically induced changes (leaching), mechanical effects and radiation effects. The waste container testing involves corrosion investigations, mechanical testing and studies of radiation effects. Testing of geologic backfill is discussed with the emphasis placed on the use of dynamic approaches to determine radionuclide migration. Backfill is chiefly investigated for its ability to retain radionuclides under different aqueous flow conditions. Finally, the different objectives for whole package testing are reviewed and compared to recent experiments started in DOE laboratories. Recommendations for further research are made in all the above areas and general types of testing for compliance purposes are identified.

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EXECUTIVE SUMMARY

A major part of NRC's program effort for high level waste materials is the continuing review of pertinent DOE programs. The purpose of these DOE programs is the development of performance data on candidate materials that may comprise a waste package. The objective of the review is to assist NRC in fulfilling its responsibility of advising DOE of the types of information needed to determine whether waste packages will meet the performance objectives and design requirements of 10 CFR 60. To fulfill this responsibility, NRC must develop an understanding of: (1) the behavior and interactions of candidate barrier materials under repository conditions; (2) the design and parameters and repository conditions that lead to failure of the waste package; and (3) the limitation of analytical and test techniques used to verify the performance of proposed engineered barriers and systems.

This report summarizes the evaluation of test development programs conducted by DOE for characterizing the performance of the waste package and package components under a variety of possible repository conditions. Testing and characterization of each component are discussed separately. Waste form testing is considered in terms of chemically induced changes (leaching), mechanical effects, and radiation effects. The waste container testing involves corrosion investigations, mechanical testing, and studies of radiation effects. Testing of geologic backfill is discussed with emphasis placed on the use of dynamic approaches to determine radionuclide migration. Finally, the different objectives for whole package testing are reviewed and compared to recent experiments initiated in DOE laboratories.

In addition to the conclusions we have reached based on our evaluation of DOE (and other) test development programs, we have identified below some of the pertinent areas where further efforts are warranted in reaching a satisfactory understanding of waste package behavior.

Waste Form Testing and Characterization

- The formation of MCC has resulted in substantial progress being made in establishing greater confidence in leach testing as the major method of evaluation for the waste form.
- Waste form leaching must be understood on a mechanistic basis. Without this understanding, no confident prediction of long term leaching behavior can be made.
- Future MCC leach tests should place greater emphasis on characterization of the waste form itself during and after leaching experiments.
- Present solution analytical techniques are not adequate for detection of many elements removed from waste forms under a variety of conditions. Development of alternative techniques (e.g., high performance liquid chromatography) should be pursued.

- More consideration needs to be given to the interpretation of leach data of forms that can be used to demonstrate compliance with the proposed NRC release rate criteria.

- To date, most mechanical testing of the waste form has centered on the quality assurance type of tests required to demonstrate stability during transportation accidents. By contrast, little attention has been given to evaluating various generic methods for the performance assessment of the waste form exposed to repository stresses over extended times.

- Possible radiation effects on waste form leachability include internal alpha decay, ionizing radiation effects, and internal transmutations. Tests under development, MCC-6 in particular, have the potential for developing the requisite information for licensing. However, the test requires qualification in several areas, particularly dose rate effects, and radiation induced stresses.

- Internal doping is the recommended method for simulating internal alpha decay in waste forms, as opposed to external ion bombardment. However, it is essential that the damage mechanisms due to each method be understood. Comparative experiments using neutron and heavy particle bombardment may be useful for this purpose.

- The density and, therefore, the internal stresses of the waste form will be affected by ionizing radiation and internal alpha decay. This will be particularly important in multi-phase waste forms. Mechanical tests should be carried out in conjunction with irradiation to high dose levels.

Container Testing

- Corrosion studies of potential container materials are, as yet, very inadequate for the requirement contemplated. This is particularly true for the more fundamental studies which will eventually be needed to demonstrate 1000 year containment. No new tests specific to the long term integrity requirement have yet been generated.

- Electrochemical corrosion studies hold some promise for use in testing for possible areas susceptible to pitting. Electrochemical experiments should, however, be done in close coordination with other types of immersion tests. Underground redox conditions should be better understood, in conjunction with such studies.

- For the quantitative assessment of catastrophic failure of the container, a fracture mechanics approach is desirable, particularly when assessing the effects of stress corrosion and hydrogen embrittlement.

- Waste package design will be very important in determining corrosion. For example, the use of various backfills will markedly alter the chemistry of the groundwater. Thus, backfills will have to be incorporated into tests at an early stage.

- Virtually no effort has been devoted to the standardization of generic methods for mechanical testing of container materials. Furthermore, stress conditions in repositories have received little attention.

- Many new techniques are available for non-destructive quality assurance tests. These include acoustic emission, eddy current inspection, radiography, dye-penetrant and helium leak detection, etc. The use of such techniques has apparently not been contemplated for whole containers and should be investigated.

- For metallic containers, radiation can, for the most part, be viewed as an environmental variable in generic corrosion or mechanical testing procedures. It does not appear that unique analytical techniques will be required to evaluate the effects of radiation in container testing.

- Perhaps the most important effects of radiation on container corrosion in the repository environment will be associated with gamma radiolysis of corrosive media (or overpack/backfill/host rock material). Radiolysis effects on corrosion may be evaluated either by carrying out all corrosion tests under irradiation or by carrying out certain generic measurements to establish worst case conditions, and subsequently testing the material under these conditions. The latter method is most convenient, but research will be required to qualify the test procedure.

Backfill Testing

- Candiate backfill materials should be tested for their radionuclide retardation properties using dynamic systems such as column experiments. Using this approach, retardation factors and diffusion coefficients can be experimentally determined under realistic chemical, thermal, hydrologic, and radiation conditions to obtain information for the comparative evaluation of backfill.

- The pore water chemistry of the radionuclide/backfill systems should be examined as a part of all tests. In cases where radionuclide breakthrough cannot be observed on a laboratory time scale, this information is absolutely necessary to determine the rate and extent of radionuclide migration. Where breakthrough can be observed, such information can allow for the calculation of radionuclide partitioning between the solid and liquid phases and can also provide mechanistic data.

- The data obtained in terms of retardation factors and diffusion coefficients should ultimately be applied to mass-balance type models. These models can be used to estimate radionuclide breakthrough times and release rates which can then be used to evaluate backfill performance in terms of the NRC criteria.

- Tests will be required to determine the effect of irradiation on backfill performance. These should include evaluation of external gamma irradiation effects, irradiation effects by sorbed nuclides on elution properties, and gas generation from dry backfill.

Whole Package Testing

- Current designs for failed whole packages are unrealistic and very limited data have been generated. The design of realistically failed components is desirable. In addition, tests on combinations of components should be considered in support of whole package tests.

- With limited experimental data, the analytical assessment of waste package performance is inevitable. Comprehensive models are desirable which incorporate both the experimental data and probabilistic descriptions.

TEST DEVELOPMENT REVIEW

1. INTRODUCTION

The prime consideration in the design of a high level waste repository is the minimization of radionuclide release to the environment. In the past, it was intended that such minimization would be accomplished by geologic isolation. More recently, however, the NRC has proposed criteria[1] which emphasize engineered barriers to minimize radionuclide loss from a repository.

This change in emphasis is closely related to the "testability" of any facility containing high level nuclear waste. While the chosen geological barriers seem likely to provide isolation under most circumstances, it is very difficult to characterize and test the performance of such natural systems. By contrast, a man-made or engineered barrier in the repository is more amenable to analysis, either theoretical or experimental, thus allowing performance to be evaluated to the limits of the system's integrity.

A major part of NRC's program effort for high level waste material is the continuing review of pertinent DOE programs. These programs are developing performance data on candidate materials comprising the waste package.

The objective of the Task 4 Review and Assessment is to assist NRC in fulfilling its responsibility of advising the DOE of the type of information needed to determine whether waste packages will meet the performance objectives and design requirements of 10 CFR 60.[1]

To fulfill this responsibility, NRC must develop an understanding of:

(i) the behavior and interactions of candidate barrier materials under repository conditions;

(ii) the design and parameters and repository conditions that affect failure of the waste package;

(iii) the limitation of analytic and test techniques used to verify the performance of proposed engineered barriers and systems. These limitations include:

a) analytical sensitivities of the measurements of chemical, physical, and nuclear properties of material test samples, leachants, corrosive agents, etc.,

b) validity and reliability of predictive models used to extrapolate short term data to long term performance,

c) scaling of non-prototype tests to repository field conditions,

d) verification of analytical procedures for integrating single component test data to whole package performance and verification of test procedures used for evaluating engineered barriers.

As a result of the understanding achieved in these areas the NRC will give guidance to the DOE via staff technical positions and periodic letters on the NRC's information needs.

This report summarizes our evaluation of the test development program organized by the Department of Energy for characterizing the performance of the waste package under a variety of possible circumstances. An interim report of this task group appeared earlier.[2] As part of this task we have identified areas where additional work is still required in reaching a satisfactory understanding of waste package behavior. Finally, we have attempted to suggest possible means by which test data could be used to demonstrate compliance with NRC radionuclide release criteria on the engineered systems. At the present time these criteria for high level waste are:[1]*

> "(a) The engineered system shall be designed and constructed, so that the waste packages will contain all radionuclides for the first 1000 years after decommissioning and for as long thereafter as is reasonably achievable, assuming anticipated processes and events, including full or partial saturation of the underground facility."
>
> "(b) ...the engineered system shall be designed and constructed so that after the first 1000 years, the rate of release of radionuclides from the underground facility will be as low as is reasonably achievable. As a minimum, the design shall not allow the annual release of each radionuclide to exceed one part in 10^5 of the maximum amount calculated to be present in the underground facility at any time following 1000 years after decommissioning."
>
> For transuranic (TRU) wastes the criterion is set as follows:
>
> "Starting at decommissioning, radionuclides present in TRU waste will be released at a rate that is as low as reasonably achievable and in no case greater than one part in one hundred thousand of the total activity present in TRU waste within the underground facility at the time of decommissioning, assuming expected processes and events."

Most concepts of a waste package consist of several components, each representing a different type of barrier to the release of radionuclides. In Figure 1.1 the likely placement of the most important of these components is represented schematically; their function is described in Table 1.1.

This report will discuss, in turn, the testing of each major component by all useful methods. This contrasts somewhat with our interim report[2] where each type of testing or characterization was considered separately. However, one of the most important considerations of this report concerns procedures by which single component tests can be used to demonstrate release

*The proposed rule (published in the Federal Register July 8, 1981) inlcludes some changes from the May 13, 1980 draft (referenced during preparation of this report) in the definition of the waste package and the statement of the performance objectives.

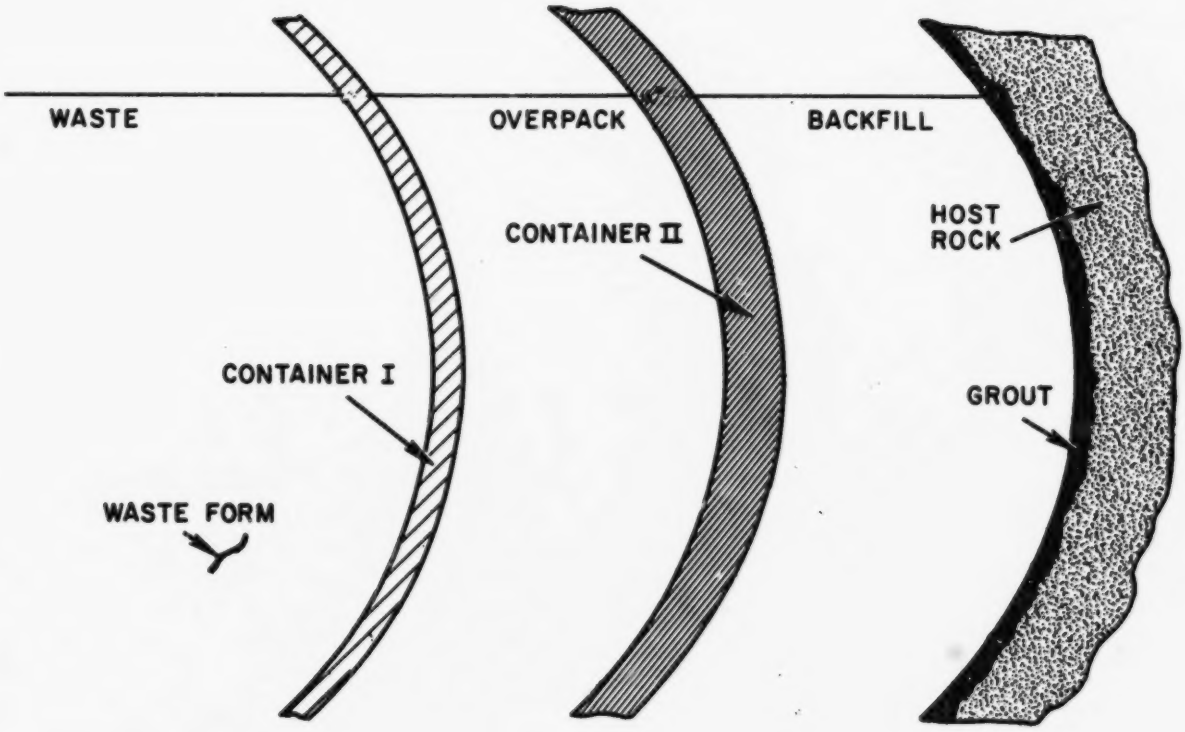

Figure 1.1. Schematic representation of components of the waste package.

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Table 1.1*

Functions of Waste Package Components

Waste Form:	Immobilizes the radioactive materials, resists leaching, powdering, cracking and other modes of degradation. Materials now being investigated are: glasses, calcines, ceramics (e.g., SYNROC), coated particles and cements.
Container:	Principal sealed enclosure around the waste form; serves as a barrier against waste form leaching and nuclide migration. Materials being considered include titanium and titanium alloys, nickel-rich superalloys (e.g., Inconels and Hastelloys), steels, copper and lead.
Overpack:	Provides an additional radionuclide release barrier, in the event the integrity of the container is breached; provides additional corrosion or structural resistance, or additional radiation shielding, if required. Overpack may be comprised of the same materials as used for backfill.
Backfill:	Placed into the emplacement hole around the (overpacked) container, acts as a sorptive medium, heat transfer agent, and plastic stress adjustment medium; it may contain oxygen-getters or chemical conditioning agents. Materials considered for use as overpack or backfill include clays, zeolites, mineral mixtures and cements.

*See Figure 1.1 for illustration of this stylized concept for a high-level waste package.

criteria placed on the entire package. Therefore, characteristics of each component, e.g., leachability, corrosion resistance, mechanical strength, need to be considered together. Following individual discussions of waste form, container and backfill testing, the possibility of whole package tests will be considered, along with methods to "sum the parts" or combine the effects of individual tests.

The inclusion of some components in Figure 1.1, as actual parts of the waste package, is open to different interpretations. While DOE considers backfill, but no portion of the host rock, to be part of the waste package, NRC at the time this report was prepared excluded backfill and host rock as part of the waste package. In this report we have included a section dealing specifically with tests evaluating the performance of backfills. The backfill performance will have a strong bearing on the corrosibility of the container surface it is contacting. Moreover, the inclusion of backfill in the waste package design will allow the potential repository license applicant much greater flexibility in meeting the release criteria.

In testing the waste package components, samples should be subjected to all possible conditions expected in a repository environment. The results of aqueous flooding of vaults constructed in salt, shale, granite, basalt and other possible materials, must be considered. These are better understood if there is some description of the time scale over which changes occur in the chemical and mechanical conditions in the repository. The repository lifetime can be divided into three periods:

(a) Operating Phase - During the first 100-150 year period the waste package will be subject to close inspection or to remote monitoring, since the repository will be still open for emplacements in the 50 year retrieval period stipulated by NRC. Container surface temperatures for 10 year HLW are calculated[3] to range from 200°C in salt to 300°C in basalt. During such a phase, any incursion of water into the waste package region should be detected and corrective action taken.

(b) Thermal Phase - During this period from 150 years to 1000 years, the heat migration from the waste through various components, and the associated thermomechanical effects, would be of major concern in any aqueous incursion. Based on thermal loadings of $20 W/m^2$, it has been calculated[3] that a high level reprocessed waste package will have a maximum surface temperature of 110°C or less, after 150 years in any geological material contemplated for a repository.

Both the temperature and the high gamma radiation field (initially 10^5 - 10^2 Rad/h) around the package will decrease substantially over the following 800-900 year phase.

(c) Geological Phase - As the temperature around the waste package returns to near-ambient (25-50°C), the original geological factors predominate. Sometime during this phase, the container may become breached, and the annual one part in 10^5 release criterion will become important. Although knowledge of ground water flow rates

during both thermal and geological phases is important, it should be easier to match flow conditions for the latter phase to geochemical data. Ground water flow rates from 10^{-12} to 10^{-3} cm/s are found in the geological formations considered suitable for repositories. Their chemical content ranges from the ultra saline brines typical of the Waste Isolation Pilot Project sites in salt domes[2] to relatively dilute sodium, calcium and bicarbonat dominated waters typical of granite and basalt groundwaters.

The environmental conditions in each possible repository medium are discussed further in the Task 1 final report on Waste Package Overview.

1.1 References

1. Code of Federal Regulations, 10CFR60, Draft, "Disposal of High-Level Radioactive Wastes in Geologic Repositories: Technical Criteria", (proposed), advance notice of proposed rulemaking. Available from the Nuclear Regulatory Commission, Washington, D. C.

2. K. S. Czyscinski, K. J. Swyler and C. J. Klamut, "NRC Nuclear Waste Management's Technical Support in the Development of Nuclear Waste Form Criteria - Task 4; Test Development Review", Brookhaven National Laboratory Report NUREG-27773, 1980.

3. "Management of Commercially Generated Radioactive Waste", U.S. Department of Energy, Office of Nuclear Waste Management, DOE/EIS-0046F, Vol. 2, October 1980.

2. GENERAL TESTING CONSIDERATIONS FOR WASTE PACKAGE EVALUATION

2.1 Introduction

This section considers the general aspects of waste package testing and acts as an introduction to the more thorough treatment of individual components given in subsequent chapters. Major types of testing and characterization for package components are discussed in this present chapter, along with the question of selecting variables which best simulate different repository environments. Interpretation of test results is emphasized, along with the problems of scaling and extrapolation.

2.2 Purposes of Testing

Test data on waste package behavior provide information on many different levels of sophistication and for quite varied purposes. On one hand, quality assurance data will be continuously required on many components for the chosen package, as well as candidate materials. Such tests are usually well established, simple procedures yielding information on the minimum acceptability of certain materials. On a second level, "screening" tests have been used to provide interim information about the relative performance of a series of materials. Finally, exploratory or advanced test methods are required which will be capable of determining reaction mechanisms. From this, long-term behavior of the engineered system will be predicted.

2.3 Modes of Testing

The prime concern in testing the waste package performance is the determination of its ability to contain and/or restrict the release of radionuclides. Testing scenarios could, in principle, be developed to study the whole package behavior in one assembly. Alternatively, single-component or multi-component tests could be devised for each different component and the results, in principle, statistically summed to provide an evaluation of the entire package. The latter approach has received by far the greater emphasis, because of the unique demands placed on the waste package integrity. The very long expected lifetime of the package practically eliminates the possibility of observing any deterioration of an acceptable package in a realistic in situ test. Moreover, such microscopic changes that would occur at the package exterior would be very difficult to monitor without disturbing the repository conditions. Uncertainty also still exists about selecting the most potentially harmful long-term conditions in which to site such a test, although detailed geological characterization studies should narrow this uncertainty.

Single component testing, by contrast, offers relatively rapid methods for partial evaluation of the package. It is assumed that quantitative single-component tests will supply a major portion of the data base with which the waste package composition will be chosen. Therefore, much of the emphasis of this report will be on methods by which single component test results can be related to criteria for the whole package and how they can be extrapolated to long-term behavior.

2.3.1 Single Component Testing

Different waste package components are degraded by different chemical and physical processes occurring over widely differing time scales. For the waste form, leachability is the prime concern. Other properties, such as mechanical strength, for example, will determine if the waste form will fracture or disintegrate easily, thereby exposing more surface area for leaching.

For the container, the most important process is breaching by corrosion. How fast the container is breached will determine when the waste form is subjected to leaching by waters from the surrounding environment. Movement of released radionuclides away from the waste form should also be affected by the condition of the corroded container.

The sorptive properties of overpack-backfill and host rock materials will control retardation of radionuclides which escape the waste form and container barriers. As in the case of the waste form, other properties will have some influence on this process. The mechanical strength of the host rock is of some concern, since fracture in the rock will provide pathways for radionuclide bearing waters to escape rapidly, essentially short circuiting the sorptive barrier. Cracking of the compacted overpack or backfill material (either thermally-induced or from local overburden stresses) can also circumvent the sorptive barrier.

The disadvantage of single component tests is that synergistic effects which occur between components are not considered. These effects can only be anticipated from prior experience.

2.3.2 Synergistic Effects

The disadvantage of single component tests is that synergistic effects which occur between components are not considered. For example, container corrosion and waste form leaching will release metallic ions to solution, which in turn may be sorbed preferentially by the backfill material, relative to the radionuclides. This preferential sorption would decrease the efficiency of the overpack in retarding radionuclide migration. In anticipation of this synergistic effect, the sorption test conditions, and their applications, would require the following modifications. The ions released to solution due to container corrosion and waste form leaching should also be included in the liquid phases used to measure the backfill sorption capacity and selectivity. Calculations to determine the thickness of backfill material surrounding the container would have to consider changes in the retardation efficiency, if sorption studies demonstrate that container corrosion products produce a significant effect.

2.3.3 Multicomponent Testing

Some mechanical and physical tests will require that combinations of components be tested together from the onset. Mechanical strength and thermal

conductivity are two specific examples where multicomponent testing would be required. In particular, the mechanical strength of the container-waste form combination under stress is an important behavioral property, since potential fracturing is of concern in repository engineering design, as well as radionuclide release.

The same reasoning applies to thermal conductivity and heat transfer measurements. Heat generated by the radioactive wastes may affect corrosion rates and sorptive behavior in the surrounding components. These tests are considered ancillary to the main testing areas to be described.

2.3.4 Whole Package Tests

Laboratory scale whole package tests would be expected to provide valuable information on the extent of synergistic effects. Post-testing analysis of a package is particularly important for revealing evidence of unexpected component interaction.

2.4 Test Variables

An ideal test would include all the pertinent variables at realistic magnitudes and time spans. However, such a test would usually be unreasonably unwieldy and long. For this reason, and for experimental convenience, leach, corrosion, and sorption tests reported in the literature were frequently performed with an arbitrary, limited number of variables. One parameter is varied at a time, often with little concern for simulating expected natural conditions. Computer-based methods to optimize the choice of variable interactions to be studied have apparently not yet been used in waste package testing.

Frequent use has been made of screening tests in the selection of candidate materials for waste forms and containers. These tests expose a wide range of material types to equivalent conditions, so that obviously poorly performing specimens can be identified. Although this approach is quite effective for demonstration purposes, it cannot usually cover the range of conditions peculiar to failure in each material.

In the sections below some variables which are pertinent to testing most waste package components are discussed.

2.4.1 Media Composition

Comparison of test results using a variety of similar generic materials often shows wide variations. For example, corrosion study results[1] show as much as an order of magnitude variation when the liquid phase was changed from sea water to brine. Another example is sorption coefficient (K_d) results obtained for a variety of soil samples and "generic" groundwaters.[2] The results show that the observed sorption varies as a function of both the liquid and solid phase compositions. Numerous other examples can

be found where test results are functions of compositional variables such as pH, redox potential and particle size.

For reliable test results, liquid phases should duplicate the expected groundwaters in the repository environment. Samples of these natural waters should be used, or simulated groundwaters prepared based on reliable analytical data.

2.4.2 Flow Rates

Contact time variations will affect the release and subsequent movement of radionuclides from the package. In the repository, groundwaters will contact the package components for varying time depending on a number of conditions, such as permeability of the host rock, temporal variations in the thermal field, etc. The contact time, or flow rate, is the most difficult variable to estimate because it will be controlled by site-specific conditions that are not easily predictable. Data from site-specific field tests has provided information useful for rough predictions of expected hydrologic conditions.

Test methodologies for leaching, corrosion and sorption (discussed in more detail in the succeeding chapters) involve static and dynamic procedures. Static tests maintain continual contact between the same solid and liquid phases during the duration of the test, while the dynamic tests involve contact with a continually renewed aqueous phase. A conservative approach to testing would require both static and dynamic testing to be performed on the package components. Dynamic tests should use flow rates which span the best available predictions of _in situ_ rates.

2.4.3 Time

The measurement of a change in property with time is, of course, most critical, since the objective is to provide a prediction of future behavior. Waste form leaching rates change drastically with time during the initial reaction stages. Even after months of reaction, there is often no indication that a "steady state" condition has been reached. Reaction times between backfill and radionuclides may also be finite, and the kinetics of uptake must be verified before any dynamic backfill testing system can be considered free of flow rate effects. Time-based effects in corrosion studies are the most difficult to quantify since initiation rates are strongly affected by surface topography and grain size.

2.4.4 Temperature

As in the case of time, test results may also be affected to a significant degree by temperature. The temperature in and around the waste package will vary as some function of the component's thermal conductivities, the waste loading and decay rate. Consequently, leaching, corrosion and sorption processes may take place above ambient repository temperatures.

It should be relatively easy to predict the likely temperature range in the immediate package environment, given initial waste loadings, thermal conductivity and heat capacities of the materials. However, it is not possible to predict at what point in the thermal history of the package it will be subjected to extensive leaching and corrosion, or at what temperature sorption reactions will take place. Consequently, testing should be performed at a number of temperatures to obtain data which span the best predictive estimates of the in situ conditions.

2.4.5 Radiation

Radiation is known to produce structural damage in a variety of materials, influence diffusion rates, and cause chemical reactions (radiolysis). These effects will be discussed in more detail in later sections. For testing purposes, it must be determined if a radiation field influences the results to a significant degree. Another significant question is how radiation effects can best be simulated in testing procedures. The container, overpacks and host rock will be exposed primarily to gamma radiation, while the waste form will also be exposed to alpha and beta radiation.

2.4.6 Acceleration of Conditions

In accelerated tests, variables are adjusted to shorten the time necessary to produce the desired effect. Such changes are only warranted when the reaction mechanisms are not significantly affected by the change in variable. Some indication of this may be determined by observing the effect of stepwise changes of the variable on the reaction rate. Temperature is the most commonly accelerated variable. In an ideal accelerated test, measurement of the rate should be obtained for several different values of the temperature. Only if the relationship between the rate and the temperature is found to follow the Arrhenius relationship over the range explored can the same mechanism be considered to be operational. A discussion of accelerated testing in relation to corrosion behavior is given in Appendix A.

2.5 Component Analysis

In addition to measuring release or retention of radionuclides by various components as functions of the test conditions, it is also essential that each individual component be examined during and after testing to determine its response to the test environment. Results of such examinations will provide information essential for interpretation of test results, in terms of modifying the components to enhance performance, and to confirm the assumptions upon which extrapolations in time are based. For example, metal coupons used in corrosion testing should be analyzed to determine the mode of corrosion and its uniformity. Predictive use of corrosion data must assume a specific corrosion mode, and predictable rates as functions of time. The types of analyses required for the components are outlined below.

2.5.1 Surface Structure

The structure of the reactive surface often determines the material behavior. Some types of glasses are known to undergo surface modifications upon leaching.[4] The nature of the altered surface will then determine the course of future behavior. In the case of glasses, the long-term behavior of a waste form may be more dependent on properties of the altered glass surface than on other variables such as redox conditions, temperature, etc. imposed by the repository environment. Extrapolation of laboratory data to long-term behavior in the field would be meaningless if the behavior of an altered form differed significantly from the original. Similar considerations apply to corrosion studies where "passive" layers may form, limiting further corrosion.

Sophisticated surface analysis techniques, such as X-ray photoelectron spectroscopy (XPS or ESCA)[5] or infrared reflectance spectroscopy (IRRS)[6] should be used to characterize the surface of tested materials. Such examinations should be a necessary part of performance evaluation for the whole package as well as its components.

Such analyses should also be a part of post-testing evaluations of whole package tests. In these cases, the presence of all the package components may create synergistic effects not observed in single component tests.

2.5.2 Microscopic Analysis

Along with surface characterization, the distribution of elements of concern throughout the package component both before and after testing will reveal the long-term behavior of the material. Multi-phase waste forms, such as coated glasses or SYNROC are examples of materials in which the phase distribution of elements can alter with reaction time, due to preferential leaching. Scanning transmission electron microscopy and ion microprobe analysis are two examples of techniques capable of resolving elemental distributions to a 1 μm resolution and detecting most elements in the periodic table. These techniques should also be used in conjunction with the surface analysis techniques to characterize the components tested singly and together.

2.5.3 Analytical Sensitivites

The degree to which test results can be applied to predict field performance and assure compliance with the limits proposed in 10CFR60 depends upon how well the test data can be scaled and extrapolated. These data manipulations in turn are dependent upon the analytical sensitivities of the test measurements. For example, the lower limit to which leach rates can be presently determined,[7] 10^{-8} g/cm^2-day, can be measured using a combination of neutron activation and gamma spectroscopy. It is suggested that this limit can be extended to the range of 10^{-10} g/cm^2-day by increasing sample size and/or neutron fluence.[7] These leach rates are generally lower than those measurable by other analytical techniques. In the case of sorption testing, radionuclides with either very high or low distribution coefficients will contain small concentrations in the liquid or solid phases, respectively.

Therefore, sample sizes and measurement techniques must be adjusted to give maximum analytical sensitivity. Clearly, the analytical methods used for measurements should be as sensitive as possible in order to produce more accurate data. Recommended techniques will be discussed at length in the appropriate sections of this text dealing with individual testing areas.

2.6 Extrapolation and Scaling

Theoretical justification for extrapolation is straightforward and specific. In order to extrapolate variable y in variable x, the functional dependence of y on x must be known and the relationship must be time invariant or accounted for.

For example, in order to extrapolate a leach rate to a temperature beyond which measurements are made, the measured leach rate-temperature relationship must be precise enough to demonstrate an explicit functional form. It must also be assumed that the relationship would not have changed if the individual leach rates were measured over times much longer than the times over which the data were obtained.

Theoretical justification for scaling a kinetic process is also specific. The geometric contributions to each and every variable affecting the rate must be known explicitly, and again, the functional dependence of the variables on geometric factors must be time invariant or accounted for temporally.

2.7 Conclusions: Summing the Parts - Total Release Rates

The radionuclide release rates proposed in 10CFR60 refer to releases from the engineered system, which comprises more than the immediate boundary of the waste packages. In order to evaluate package performance in terms of the underground facility, package release rates are required as a first step. These rates may be estimated in one of two ways -- (a) from results of whole package testing, and (b) from the integration of results from single component tests.

Results from whole package tests are certainly most desirable, because the problems of integrating data from single tests are avoided, along with the problems caused by synergistic effects. However, the wide range of conditions which would have to be studied, the very difficult problems of acceleration and the non-availability of appropriate *in situ* analytical techniques seem to preclude the use of whole package tests for quantitative use.

In lieu of using whole package test results, single component results must be used in the qualification process. The final product of single component testing is a collection of data unique to each of the components. Corrosion and leach rates are reported (Table 2.1). These results must then be combined to produce a release rate for the total engineered system. Here again, more than one approach can be taken. In each of these approaches, an initial radionuclide loading in the waste form must be assumed before the data can be evaluated in terms of release rates.

Table 2.1

Units of Measure for Leach, Corrosion and Sorption Testing

Component Test	Parameter	Units
Waste form-leaching	radionuclide specific leach rate per unit area	g/cm^2-day
	mass leach rate per unit area	g/cm^2-day
	volume leach rate	cm^3/day
	fractional release rate	yr^{-1}
Container corrosion	mass corrosion rate	g/day
	volume corrosion rate	cm^3/day
	pit corrosion rate	cm/day
Host rock-overpack sorption	sorption coefficient (K_d)	mL/g

The most conservative approach would require that several of the components pass individual standards high enough to meet or exceed the total package release rates. This would require waste form leachabilities to be low enough so that their release rates satisfy the total package requirements. Containers must resist breaching for a thousand years, and the sorptive capacity of backfill must be high enough to contain the entire waste package radionuclide inventory after leaching has begun. This approach would assure that the whole package standards are met, and also avoids the problem of integrating single component test results into a whole package release rate.

An alternative "strong link" approach would allow one or more of the components to fall below the standards for the whole package. The waste package would be acceptable as long as at least one component can be demonstrated to meet, or exceed, the total package criteria. This approach avoids the problem of integrating data for component tests into whole package behavior, but provides only qualitative assurance of package stability if an unexpected failure of the one component occurs.

If it is decided that the "strong link" approach should not be used, the integration problem is thus unavoidable. In order to predict whole package behavior in this case, the testing of each component should be more extensive.

2.8 References

1. J. W. Braithwaite and M. A. Molecke, "Nuclear Waste Canister Corrosion Studies Pertinent to Geologic Isolation", Nuclear and Chemical Waste Management, 1, 37 (1980).

2. L. L. Ames and D. Rai, "Radionuclide Interactions in Soil and Rock Media", Environmental Protection Agency Report, EPA 52D/6-78-007 1978.

3. B. R. Erdal, W. R. Daniels, J. L. Thompson, R. D. Aguiler, B. P. Bayhurst, C. J. Duffy, F. O. Lawrence, S. Marstas, P. Q. Oliver and K. Wolfsberg, "Laboratory Studies of Radionuclide Distributions Between Selected Ground Waters and Geologic Media", Los Alamos Scientific Laboratory Report LA-UR-79-534 1978.

4. D. M. Sanders and L. L. Hench, "Mechanisms of Glass Corrosion", J. Am. Ceram. Soc. 56 (1973).

5. L. R. Pederson, M. T. Thomas and G. L. McVay, "Application of ESCA to Corrosion Studies of Glasses Containing Simulated Nuclear Wastes", J. Vac. Sci. Technol. 18, 732 (1981). (Pacific Northwest Laboratories preprint PNL-SA-8687).

6. D. E. Clark and E. L. Yen-Bower, "Corrosion of Glass Surfaces", Surface Sci., 100, 53 (1980).

7. K. F. Flynn, L. J. Jardine and M. J. Steindler, "Method for Determining Leach Rates of Simulated Radioactive Waste Forms", in Radioactive Waste in Geologic Storage. S. Fried, Ed., A.C.S. Symposium Series V.100. (American Chemical Society, Washington, D. C.), 1979, pp. 115-128.

8. D. D. Hostetter, R. J. Serne, A. J. Baldwin and D. M. Petric, "Status of Sorption Information Retrieval System", Pacific Northwest Laboratories Report PNL-3528, 1980.

3. THE MATERIALS CHARACTERIZATION ORGANIZATION - ITS ROLE IN TEST DEVELOPMENT

Since the writing of the Interim Report[1], much progress has been made by the Department of Energy (DOE) towards the development of standard tests for the characterization of the components of the waste package.

In late 1979, the Office of Nuclear Waste Management of the Department of Energy established the Organization of Waste Materials Characterization. The Materials Steering Committee (MSC) is the administrative head of the organization. Among other duties, it is to review and approve charters and the organization of the following:

Materials Characterization Center (MCC) established at Pacific Northwest Laboratory (PNL)

Materials Review Board (MRB) managed by Argonne National Laboratory (ANL)

Independent Measurement Standards Laboratory (IMSL) at National Bureau of Standards (NBS)

The MCC is to provide the data base on all components of the waste package which will form the basis for waste materials specifications, testing standards, quality control procedures, and licensing action. The data are obtained at the MCC and other sites by documented test procedures which are developed by the MCC and approved by the MRB. The data and approved test methods must be representative of the conditions expected in the waste management system including interim storage,transportation, engineered barriers, disposal, and the interaction with the host environment. One emphasis of the Task 4 report is to review and assess the test development program being developed by the MCO.

A preliminary plan[2] which outlines the basic test methods for waste forms and engineered barriers includes the following: (a) waste forms - chemical durability (leaching), radiation stability, thermal stability (volatility, phase stability, gas generation), mechanical properties (impact test, compressive strength test), sampling (specimen description and analysis); (b) container and overpack - corrosion, mechanical and physical properties, stability (radiation and thermal effects); (c) backfill - water interaction, mechanical and physical properties.

A compilation of the approved test methods and materials data will be published in the Nuclear Waste Materials Handbook. The Handbook, which will be periodically updated by the MCC, will have three sections: (a) procedures, (b) data and certified data, and (c) supporting material will be modeled after the Nuclear Systems Materials Handbook. The first issue is due in early FY 1982.

The main functions of the MRB are (a) to examine the test procedures and materials data on waste package components developed and documented by the MCC with respect to their acceptance criteria, technical quality and merit, applicability, etc., (b) to certify the test procedures or data to be used in the technical community, (c) to review periodically the programs of the MCC.

IMSL will promote consistency and accuracy of data used in nuclear waste management. Specific functions include:

- Development of selected test methods and procedures.
- Provision of standard reference materials, research materials, standard reference data, and round robin tests and other inter-laboratory comparisons.
- Performance of selected tests and evaluations.
- Performance of research and development (R&D) to assure that standards activities have a firm scientific basis and to assure that cognizance of related R&D, both domestically and internationally, is maintained.
- Independent scientific peer review of selected measurement and standards related science and technology developed by other laboratories, including the MCC.
- Arbitration of data or analytical discrepancies in areas where the IMSL has the requisite competence.
- Provision of technical assistance, upon mutual agreement, to the Department of Energy's Materials Review Board.
- Liaison with national and international standards organizations.

3.1 References

1. K. S. Czyscinski, K. J. Swyler, C. J. Klamut, Brookhaven National Laboratory Report, "NRC Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria: Task 4: Test Development Review." Brookhaven National Laboratory, NRC-NUREG-27773, Interim Report, May 1980.
2. "Composite Quarterly Technical Report, Long-Term High-Level Waste Technology, October-December 1979," Savannah River Laboratory Report DP-79-157-4, 1980.

4. CHARACTERIZATION AND TESTING OF THE WASTE FORM

4.1 Types of Waste Forms

The Task 1 report describes in detail the high level waste forms which have been considered in the recent past. In this report we will be concerned mainly with those waste forms which have a reasonably high probability of selection by the Department of Energy. These are:

- glasses
- polycrystalline ceramic forms (SYNROC, supercalcines and titanates)
- coated particles
- spent fuel

4.2 Testing of Chemical Properties

4.2.1 Leaching Mechanisms

A principal means of release of radioactivity from a nuclear waste repository is by dissolution of the radionuclides in the waters of the environment. This can happen only through attack of the solid waste form by groundwaters. The mechanisms by which such a release occurs are leaching (selective release of certain elements) and congruent dissolution of the waste form. Both of these are important to study; all mechanisms must be well understood in order to develop a capability to scale and extrapolate laboratory data to repository conditions.

4.2.1.1 Glass Leaching Mechanisms in the Initial Attack of Alkaline Silicate Glass by Water

By far, the most studied waste form is glass. At least three different stages are involved: a) The first is ion exchange of hydronium (H_3O^+) or hydrogen (H^+) ions from the water with alkalai ions, e.g. Na^+, in the glass.[1,2] b) The second is the partial hydration of the silicon - oxygen network of the glass,[1] thus forming a partly protective layer, depleted in alkalis, on the surface. This layer would not be protective in some waste glasses because of the low density of matrix elements. c) In the third stage, as the pH is increased due to an increased OH^- concentration, the silica network itself is attacked,[3,4] causing the dissolution of the glass into the contacting solution and thus greatly accelerating the corrosion process.

Ion exchange is a diffusion-controlled process which leads to selective leaching and is generally rate controlling when the solution in contact with the glass has a pH $\leq$9. Therefore, in the early stages of corrosion the amount leached varies with time. Network dissolution is a surface reaction involving the breaking of structural Si-O-Si bonds and is rate controlling when the pH $\geq$9. At that time, all the species in the glass dissolve simultaneously. Therefore, as the reaction continues for a long time and network dissolution becomes predominant, the rate becomes linear with time.[5]

In more complicated systems, the absence of one or more steps described above leads to another classification of corrosion modes in view of the apparent overall dissolution. The glass may: (a) react with the corrosive materials to form new compounds on the surface; (b) be preferentially dissolved leaving a leached surface layer; (c) be totally dissolved continuously exposing fresh glass. Workers at the University of Florida[4,6] extended this concept to five types of surfaces (Figure 4.1) of a silicate glass and correlated these to its durability. A type I surface undergoes only a hydration reaction, and that to a depth of several tens of atomic layers. Vitreous silica exposed to neutral pH solutions has a type I surface. A type II surface possesses a silica-rich protective film due to selective alkali ion removal. A glass with this type of surface is reasonably durable. Two layers of protective surface films are characteristic of Type III: the outer layer is enriched in Al_2O_3 and CaO due to reprecipitation, the inner one is enriched only in SiO_2. Such glasses are very durable in both acid and alkali solutions. Type IV glass surfaces also have a silica-rich film, but the silica concentration is insufficient to protect the glass from rapid attack by dealkalization or network dissolution, resulting in poor durability. A glass of Type V undergoes uniform attack losing considerable quantities of all ions into solution.

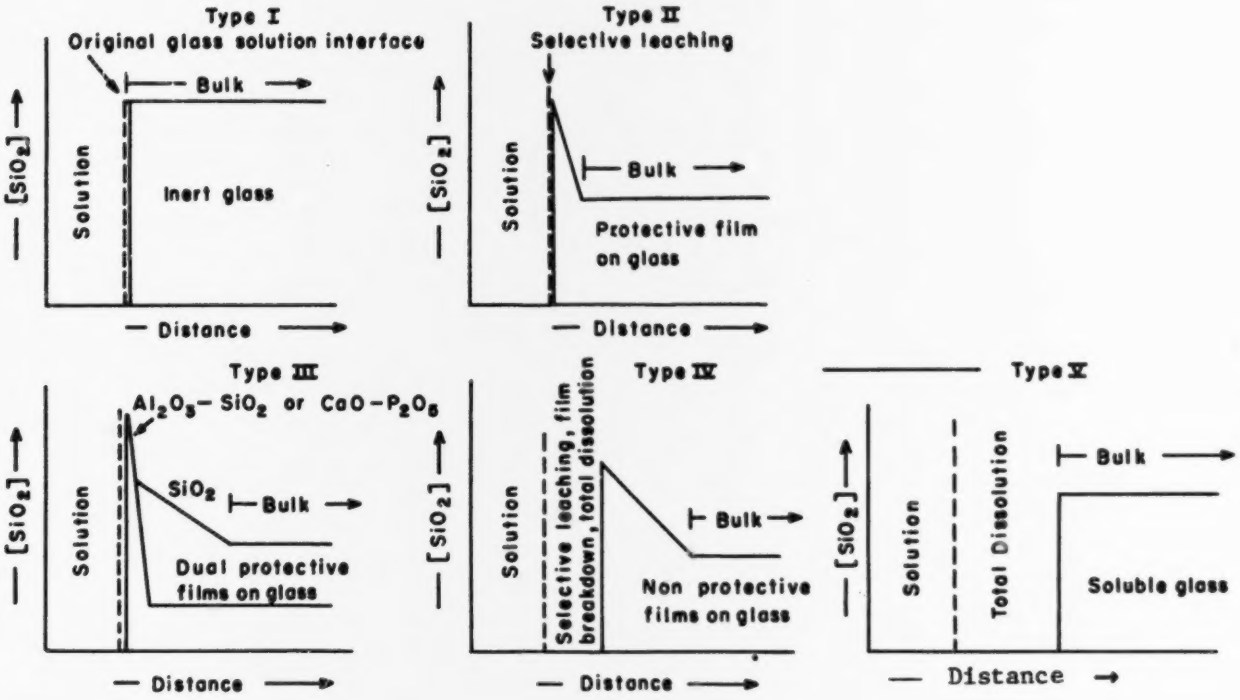

Figure 4.1. Five types of surface films developed during the leaching of silicate glasses.[4,6]

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The reaction process becomes more complicated when the glass is exposed to autoclave conditions. Clark, et al.[7] have studied the leaching of zinc borosilicate simulated nuclear waste glass. Although selective leaching and network dissolution were found to occur, there was in addition the formation of a surface crystalline phase. The presence of these crystals is thought to affect the kinetics of corrosion.

As the number of elements incorporated into the waste form increases, so does the complexity of the leaching mechanisms. Kenna, et al.[8] have reported cyclic leaching patterns resulting from long term (two years) Soxhlet leach tests on simulated nuclear waste loaded glass and titanate ceramic. The cyclic effect was greatest for the Battelle glass and lowest for the ceramic. Also, hydrothermal reaction of many waste glasses containing rare earths results in copious reprecipitation of oxides such as CeO_2, Dy_2O_3 and Nd_2O_3, due to their hydrolysis at these temperatures.[9]

Based on recent work done at PNL on solution chemistry of the actinides, it is very likely that the solubility of these radionuclides limits their release from waste forms under repository conditions rather than kinetic factors. Consequently, in addition to determining conditions which affect leachability, the study of factors which determine inherent solubility should also be emphasized for most actinide containing glasses.

4.2.1.2 Multicomponent Crystalline Waste Form Leaching Mechanisms

In the case of waste forms of multicomponent crystalline phases and multiphase mixtures, much less is known about the leaching mechanisms than for glass. Before any predictions of overall stability can be made, each individual phase must be well understood. The phases should be studied separately, as well as in assemblage, and a knowledge of their kinetic behavior in solution is important. Some phases have shown higher leachability than others. Even if the phases are found to be relatively stable to leaching, additional effects due to selective leaching at high energy grain boundaries, amorphous-crystal phase boundaries, microcracks caused by inclusions, or segregation along grain boundaries, must be explored. Knowledge of these microstructural related factors is necessary in order to understand the mechanisms and kinetics of leaching of this class of waste form. There is almost no information available[10] on the behavior of these multicomponent phases and their interactions on which to build a data base which is needed to compare actual behavior to predicted behavior. This situation is being improved somewhat by a number of research programs which have been started in this country at Sandia, Argonne and Lawrence Livermore Laboratories. So far most of the leaching results are from short term tests although some long term leach test data is beginning to appear in literature. For example, Coles' and Bazaan's[11] data on SYNROC leaching suggests that more than one leach mechanism might be operating since the leach rates vary over several orders of magnitude during the initial period and do not approach a constant rate until after 20 to 40 days of test duration.

4.2.1.3 Spent Fuel Leaching Mechanisms

One of the major differences between leach mechanism for dissolution of glass or ceramic waste forms on one hand and spent fuel on the other, is the strong dependence of UO_2 dissolution on dissolved oxygen concentration (solution Eh).[12] This appears to result from the participation of a higher valence state (U^{+6}) in the dissolution process.

Although it is possible to study UO_2 dissolution under some reducing conditions in an autoclave, it is quite difficult to simulate the very low dissolved oxygen solutions typical of a flooded geologic repository after sealing.[13] Therefore, many experimenters are turning to electrochemically assisted oxidation and dissolution techniques to understand the processes involved in the dissolution of UO_2 and fuel rods. Electrochemically assisted oxidation is capable of much greater control over both the solution Eh and the instantaneous measurement of the dissoltion rate.

Studies to date have utilized single crystal UO_2, doped UO_2 pellets and spent fuel samples. Single crystal UO_2 is used to determine uranium dissolution from different crystal planes while controlled doping of pellets is used to investigate grain boundary effects. Solutions used have been distilled water, sodium bicarbonate and WIPP brine with temperatures up to 70°C. With large quantities of dissolved oxygen, electrochemical studies give initial high dissolution rates of approximately 1×10^{-4} g/cm^2-day for uranium at 25°C,[76] which at longer leaching times becomes much lower. This has led to the postulation of the following mechanisms:

1. In the early stages, UO_2 oxidizes to a thin surface layer of U_4O_9 and subsequently goes into solution as a uranate.

2. At longer periods and/or higher temperatures, even higher valence uranium oxides will form on the surface due to uranium back-precipitations. These form a porous film which nevertheless results in an overall decrease in the overall rate of uranium dissolution.

Surface techniques, combined with electrochemical methods, are important for elucidating the particular structure formed during dissolution. X-ray photoelectron spectroscopy has been used to follow the evolution of the U^{+4}/U^{+6} ratio on the surface film of a UO_2 electrode.[76]

The electrochemically assisted dissolution of spent fuel samples is being investigated at PNL.[14] Initial results show that the open circuit potential for a fuel element surface in any of the groundwater solutions is significantly higher than for UO_2 thus indicating that the spent fuel surface has been heavily oxidized during storage. Initial dissolution rates have been determined to be approximately 1×10^{-5} g/cm^2-day.

4.2.2 Leaching Variables

Kinetic factors that influence leachability may be categorized as system related, leachant related or related to the solid being leached.[15]

The most important system related factors are: temperature, radiation environment, ratio of surface area of the solid to leachant volume (SA/V), occurence of wet-dry cycling and pressure. Leachant factors include composition, pH, Eh, oxygen and carbon dioxide fugacities and flow or replacement frequency. Important properties of the solid are composition (elemental, phase, matrix homogeneity), porosity and surface condition (i.e. method of surface preparation).

It is beyond the scope of this document to discuss all the variables and their interactions as they affect the leachability of various waste forms. Many interactive studies have been performed and their results reported in literature. Only a few of the important variables will be mentioned here and the studies cited from literature are used only as examples of the wealth of information available.

4.2.2.1 Time

As mentioned in Chapter 2, the final objective of the leach test determines the length of time required to carry it out. For "scoping" or comparison tests, much less time is required than for studying mechanisms for the purpose of long term predictions.

Leach data typically show high release rates for the initial portion of the test, followed by gradual decrease, often approaching a constant rate with time. For example, Walker, et al.[16] performed long term leach tests on waste glass at 22°C buffered at pH 7 and pH 9, and found the rates to decrease for the first 50 to 100 days. Only a small decrease or none at all was found during the subsequent 700 days. In some cases, fluctuations in leach rates with time have also been observed;[8,17] these could be attributed to changes in leaching mechanisms or spalling of the protective surface layer.

One phenomenon which could affect long term behavior of the waste form is possible alternating periods of hydration and dehydration of the glass surface arising from intermittent repository flooding. It is likely that each subsequent hydration would require the same period to establish a steady state, because drying of any protective surface film would cause it to crack and lose passivating characteristics.[18] Any physical movement or displacement of the surface film is known to affect the surface film characteristics.

At present, little information is available on the long term behavior of waste forms other than glass, although some tests have been started in the last few years.[19] For example, researchers at ANL[20] have observed in the leaching of SYNROC that cesium leaches much faster (about four orders of magnitude) than the matrix elements. While cesium leach rates do decrease with time, they do so at approximately the same rate as for borosilicate glass. Coles and Bazan[11] found the leach rates for SYNROC to approach a constant rate after 20 to 40 days of testing.

It is very important that leach tests be sufficiently long so that steady state conditions can be defined, both with respect to solution concentration changes and solid state changes.

4.2.2.2 Temperature

It should be relatively easy to predict the likely temperature range in the immediate waste package environment, given initial waste loadings, thermal conductivity and heat capacities of the materials (see Chapter 1). However, it is not possible to predict at what point in the thermal history of the waste form it will be subjected to extensive leaching and corrosion. Consequently, testing should be performed over a range of temperatures to obtain data which span the best predictive estimates of the in situ conditions. As discussed in Chapter 1, repository temperatures of 110°C or less are predicted for the thermal phase of the repository lifetime. This means that test temperatures higher than 110°C should only be necessary for the purpose of test acceleration or for simulating an extraordinary event resulting in a thermal excursion.

Increased temperature generally increases leach rate[21,22,23] but this is not always the case.[24,25] An exponential relationship between the apparent leach rate and temperature has been noted for a number of waste forms including some glasses, ceramics, individual crystalline components[26] and various carbon coatings.[27]

In the case of glasses, the quantity of alkali extracted in a given period of time increases with increasing temperature. The type of reactions which control the release of radioisotopes of waste glass also are affected by temperature. For most silicate glasses, the quantity leached in a given time is nearly double for every 8°C to 15°C rise in temperature and the reaction rate increases by a factor 10-100 for every 100°C increase in temperature, depending on the compositon of the glass and the type of alkali ion. Some workers[28] have attempted to express the temperature dependence of alkali extraction in terms of the Arrhenius equation. However, it is not easy to assign a single activation energy, since alkali extraction is always associated with pH changes and these depend, not only on the quantity of alkali released, but also on that of silica. Further, below approximately 80°C, a siliceous layer forms on a glass which acts to retard further leaching. Temperature has a large influence on the gel layer composition. Gel films formed at high temperatures (80°C) have a high degree of hydration and a lower protective ability. Thus temperature is considered the main parameter in evaluating the ability of the film to act as a protective barrier.[29] Metasomatic reactions, in which new crystalline compounds form from some of the glass constituents, can also occur at the glass surface, particularly at elevated temperatures.[7] Such complications make it difficult to theoretically define a single rate-determining step in a given temperature range. Nevertheless, for a large number of nuclear waste glasses, the apparent leach rate follows the single activation Arrhenius equation.[30,31]

The individual phases that make up a crystalline waste form have, in some cases, limited ranges of stability at different temperatures and pressures. It is therefore necessary that phase relations of the waste form water system be known before comparisons of leaching rates at different temperatures can be made. If a crystalline waste form is stable in the presence of an aqueous medium, then the dissolution process seems to follow an Arrhenius equation.[26]

Compared to borosilicate glass, the leach rate of SYNROC does not increase greatly with temperature. Reeve, et al.[32] observed the overall leach rate

of SYNROC to increase by a factor of 25 over the temperature range 45-300°C whereas the rate for glass increased by a factor of 250. Leach rates for cesium and strontium from SYNROC followed the Arrhenius equation. Studies at ANL[20] also show that leach rates for cesium as well as matrix elements from SYNROC are not as strong a function of temperature as from borosilicate waste glass. Similar observation was made by Coles and Bazan.[11] They found temperature dependence for leaching to be greatest for cesium (almost a factor of ten), while only minor temperature effects were observed for other elements between 25 and 75°C. In the case of one single phase material, Cs-Hollandite, no significant temperature effects were observed.

A change in temperature may alter other variables which would obscure the temperature relationship. For example, a change in temperature may change solution composition by changing the solubilities of gases such as CO_2 and O_2 in the solution and the pH of the solution. Therefore, if the effects of temperature are to be studied it is important to keep the composition of the solution constant. This would be especially important in accelerated testing.

Reliable temperature dependence data for spent fuel leaching are not yet available.

4.2.2.3 Flow Rate

Groundwater flow rates in the repository are difficult to predict. It is therefore important that the whole range of flow rates be explored in a testing program. The MCC has taken this into consideration; its set of five standard tests range from static to high flow conditions.

As discussed above (4.2.1.1) for glasses, under very low flow or static conditions, the pH of the solution increases due to a build-up of alkaline leach products. The leach rate will increase until enough dissolved silica produces saturation, thus retarding the leach rate. Unfortunately, most groundwater flows predicted for hard rock repositories are so low that they are difficult to reproduce in a laboratory. In the U.S. program where many different host rocks are being investigated, reference flow rates range from 10^{-4} to 10^{-8} cm/sec.[33] Therefore, static tests (MCC-1) and low flow tests[34] are believed to be the best for reproducing the most probable repository condition.

Leach tests should also be performed under "maximum risk" conditions. In the case of glass, at a moderate flow rate of unbuffered solution, the initial leach rate would depend on the pH of the solution, but as leach products of the glass accumulate, the pH would eventually be controlled by the dissolution products. If, at the same time, the flow rate is high enough to keep the system from reaching saturation, this could represent the condition for the highest rate of corrosion. However, should re-precipitation of insoluble hydroxides, hydrated oxides or silicates at high pH occur, radionuclide release to the environment could be retarded to such a degree that maximum risk conditions would correspond to the situation where the pH remains low and the rate of mass flow is high.[35] At very high flow rates, the leach rate would be controlled by the pH of the medium and the stability of the dealkalized layer.

On the basis of the above discussion, one would expect that major differences should have been determined between high flow and static conditions. This, however, has not been the case to date. There seem to be additional factors which may complicate the influence of flow rates on leaching. For example, Coles, et al.[34] found insignificant dependence of leach rates on flow rates in most cases when they measured the leach rate of various radionuclides from glass at 25°C. Weed, et al.[25] measured the leach rates for ^{237}Np and ^{239}Pu and found them to increase with flow rate at high temperatures, but to be approximately independent of it at 25°C. Further study is therefore necessary before any confidence is possible in extrapolating the effects of ground flow measurements on long-term repository isolation.

4.2.2.4 Solution Chemistry

In the past, the use of leaching solutions varying in composition from deionized water through "generic groundwaters," to waters recovered from specific natural environments, and the use of a variety of physical forms of the solids leached have made extensive intercomparisons of published test results very difficult. This problem is being resolved by the MCC tests in which the composition of three standard leach solutions (reagent water, silicate groundwater, salt brine) and the size, shape and methods of surface preparation of the sample to be leached have been specified.

An understanding of the effects of solution composition on the waste form is important since the leach rates for identical materials are known to be affected by the composition of the leachant[25,36,37,38] and leach rates for individual elements vary in the same material.[22,25,34,39,40] Experiments have also shown that certain species, when added to the leaching solution, can improve the overall chemical durability of glasses in contact with the solution. It was found that Al^{+3} and Ca^{+2} improved the resistance of some glasses against network dissolution while Cu^{+2} had the opposite effect.[41]

The most important solution parameter known to affect leaching at a given temperature is the pH of the solution. Diffusion-controlled leaching will tend to be reduced with increasing pH because of the decreasing concentration of H^+ and hence H_3O^+. However, matrix dissolution in the case of silicate minerals and glass would increase at high pH (≥ 9) because of an accelerated attack on the Si-O bonds by OH^-. Therefore, in the leaching of a glass, which generates high pH leachates, rare-earth, transition elements and actinides are leached at lower rates than the silica matrix. Leach rates are also increased by low pH leachants since more H^+ is available for ion exchange in acidic solutions.[30,36,41] Surface reaction mechanisms are also pH dependent. In the case of UO_2 in spent fuel, both low and high pH would enhance its dissolution.

Sometimes it is useful to be able to control the pH in order to see the effect of other solution factors on leach rate. Such tests could also simulate high dilution or rapid flow tests and lower dilution conditions where the solution would contain a high level of buffering solutes. In addition, carrying out tests at constant pH levels provides information for modeling the corrosion process. Researchers at Catholic University of America[42] have done extensive work in developing buffer systems suitable for leach tests in the pH range of 2 to 10.

The rate of change in solution pH is controlled by the ratio of surface area (geometric) of solid to volume of leachate (SA/V). As the SA/V increases, more ion exchange will take place per unit volume of solution and the concentration of species in the solution will increase. Consequently, the pH will also increase.[28,41] As discussed above, increase of pH $\geq$9 will lead to matrix dissolution, but at high SA/V this would finally also lead to solution saturation. Therefore, although the pH is high, only a small amount of glass is dissolved.

The same would be true for species other than the matrix elements. Chemical back reactions or reprecipitation are responsible for the decrease in leach rates of high SA/V. These phenomena are all related to saturated solution effects at the glass/solution interface. The highest leach rate would occur at a SA/V where pH is high but solution saturation is inhibited by high solution volume.

Under static or low flow leaching conditions, the pH of the leach solution is also strongly affected by the nature of the glass constituents. For example, high amounts of iron in the glass will lower the pH and will lead to less precipitation of rare-earth elements at the glass-leachate interface.[43]

With the exception of spent fuel studies,[14] very little effort has been directed to understanding the role of Eh on waste form leach rate. The need for more work in this area has been recognized by DOE contractors.

Changes in Eh will have a most marked effect on waste forms whose dissolution mechanism involves a change in valence state. This is, of course, very important for spent fuel elements of UO_2, which must undergo oxidation to U^{+6} in order to enter solution. Aside from this, any waste form containing multivalent actinides such as uranium, neptunium, and plutonium, or other multivalent elements such as technicium, ruthenium, and molybdenum is likely to be affected by changes in groundwater Eh.

In view of the above discussion, although standard leach solutions are necessary for comparative testing and mechanistic studies, for final testing the leachates used should duplicate the waters expected in a repository. The waters should be equilibrated with the overpack-backfill material prior to contacting the samples and some tests should be performed with solutions which also contain species from would-be breached containers. Leach tests with backfill and container materials present are necessary, but equally important is a better overall understanding of solution chemistry produced by these interactions. These types of tests will be site-specific, and therefore cannot be performed until the site and the rest of the waste package components have been chosen.

4.2.2.5 Surface Area

The determination of the surface area of the waste form being leached is important in order to obtain normalized leach rates which may then be used to compare the performance of different waste forms.

In some cases, the geometric surface area of samples, calculated in the case of powders and measured in the case of cores and monoliths, has been used

in the generation of leach data. This represents a useful first approximation of the surface area but, due to voids, steps, pores, and other surface imperfections, the actual sample surface area is greater than the geometric surface area. Thus, geometric measurements would underestimate the actual surface area available for leaching and therefore give a conservatively high leach rate (which is expressed per unit area). This is acceptable if the leach rates of two identically prepared samples of the same waste form are being compared, but not if the comparison is being made between two samples with different surface characteristics. The difference in the surface area could be intrinsic or could appear to have been introduced by the sample preparation technique. Ceramic waste forms appear to have a higher intrinsic surface area than glass due to their crystalline structure and therefore, in the case of identically sized monoliths of SYNROC and glass, the SYNROC sample would have a significantly greater surface area.

In other cases, surface area has been measured by means of gas adsorption. This technique lends a greater degree of accuracy to waste form evaluation because it accounts for many of the fine surface features ignored by geometrtic measurements. Several techniques are available for the determination of surface area by gas adsorption and for most part, these are based upon BET adsorption theory.[44] The use of BET surface area measurements generates more realistic and reproducible leach data.

These points are illustrated by experiments performed by Coles and Bazan[11] on SYNROC and PNL 76-68 borosilicate glass. A comparison was made between the Krypton BET and geometric surface areas of small SYNROC cylinders. The BET area was greater by a factor of about 27 and hence the leach rate of the SYNROC was correspondingly reduced. In the case of glass, the BET area was found to be a factor of 10 greater than the geometric area. Therefore, it is important to exercise caution in comparing leach rates of different waste forms whose surface areas have been measured by different techniques. A good example of this has been the recent comparison of leach rates for SYNROC and borosilicate glass where the former surface area was measured by BET and the latter by geometric methods.[45]

4.2.3 Analytical Methods for Leach Testing

The leach rate testing of the earliest glass waste forms in the 1950's brought with it the requirements for sensitive and precise analytical techniques which could detect the accumulations of the most mobile elements in the leachate. The present day emphasis on mechanistic understanding of as much of the leaching process as possible requires that a number of different elements in the waste form matrix be monitored during their dissolution. Moreover, characterization of changes in the waste form itself must be made if leaching is to be understood on a mechanistic basis. Present day tasks are pressing the analytical sensitivities of most modern methods to their limits; therefore, there is a clear need for development of new techniques and procedures, which will allow measurements of a greater number of elements to much lower detection limits. In three sections below, leach solution analytical methods, solid characterization methods and sampling difficulties are discussed.

4.2.3.1 Leach Solution Analytical Methods

It is useful to calculate the analytical sensitivity required for each element being leached from a waste form under low temperature conditions. Leaching rates of 1×10^{-6} g/cm^2-day have been measured for some of the more durable waste forms in 25°C water. Based on the use of the MCC-1 static leaching test with a 100 ml volume of leachant and a 3 day leach period, analytical sensitivity ranging from 10^{-2} µg/ml to 10^{-6} µg/ml would be required to determine most elements removed from the matrix during a congruent dissolution. The wide range of sensitivities required results from the different concentrations of elements (20% to 0.01%) in the waste form matrix.

There are few trace analytical techniques which are capable of reaching the 10^{-2}-10^{-6} g/ml range for many elements. Most previous non-radioactive leach testing has been carried out under accelerated high temperature conditions and only the major elements have been detected. A number of possible approaches are discussed below for reaching the higher sensitivities necessary for a full characterization of the leaching behavior under more ambient conditions.

(a) Molecular Spectrophotometry - Many elements in aqueous solution can be detected at trace levels since they react to form colored organometallic complexes. Few[46] of these complexes can be used to detect levels as low as 10^{-3} µg/ml. When this fact is combined with the degree of cross interference and the often tedious and exacting procedures involved, little likelihood can be seen for colorimetric procedures assuming an important role in leach testing.

(b) Atomic Absorption Spectrophotometry - Several elements typical of the waste package are detected with just adequate sensitivity using flame methods (e.g. sodium, magnesium, and calcium). Other elements such as iron, zinc, tellurium and antimony can be analyzed in a satisfactory sensitivity range if graphite furnace atomization is used. This latter technique, however, is more susceptible to interference effects and is slower and more difficult to use.

(c) Flame Emission Spectroscopy - This technique has sufficient sensitivity to monitor potassium and cesium concentrations under most of the conditions outlined above.[46]

(d) Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)- The technique has been adopted as the major solution analysis tool in the DOE waste management program, because of its fairly high sensitivity to typical waste form elements, low degree of inter-element interference, and good capability for rapid multi-element analysis. Detection limits for strontium, zironium, titanium, boron and yttrium are sufficiently good to allow their detection under most leaching conditions. Rare earths and actinides, such as neodymium, thorium, and cerium are detectable under some of the leaching conditions.[47]

(e) Neutron Activation Analysis - When a high fluence of neutrons is available for analytical purposes, activation analysis can provide

data with quite satisfactory sensitivity for a number of typical fission product elements, e.g. zirconium, cesium, barium, strontium, europium and scandium. Leach data can be obtained most conveniently and precisely by activation of the waste form prior to leaching followed by gamma spectroscopic analysis of the solution. There is some concern, however, that neutron damage to the waste form may alter the leach rate, particularly in multi-phase waste forms. Recently, a comparison was made of leach data from a neutron activated waste form with data obtained by activating the original solution.[48] Both data sets agreed within 20%. Analytical interference, however, also is expected to result from the large number of rare earth gamma emitters present in the leachate; this may necessitate time consuming chemical separations.

(f) Liquid Chromatography - High pressure liquid chromatography (HPLC) with a variable wavelength detector has been shown to be very successful for separation and detection of a number of metal ions in the range of 10^{-3}-10^{-6} µg/ml.[49] The determinations of both rare earth and transition elements have been reported in natural and reactor coolant waters.[50] Thus HPLC appears to have certain potential advantages in the analysis of leach solutions, which require high sensitivity and rapid multi-element capability.

(g) Mass Spectrometry - Highly accurate and sensitive measurements can be made with isotope dilution techniques. This has been highly developed for actinides,using preconcentration techniques with ion exchange resin beads, so that the limits of detection are around 10^{-3} µg/ml for uranium and 10^{-6} µg/ml for plutonium.[51] These facilities are available in most nuclear laboratories, but the procedure becomes quite expensive if multiple analyses are desired.

The present state-of-the-art in leach water analysis lies in the use of ICP Spectroscopy and Neutron Activation Analysis. Both of these methods could be extended using solution concentration techniques (evaporation or selective precipitation). In addition, development work on HPLC techiques appear very worthwhile, yet for the moment is overlooked. Neutron activation techniques and seperations also require more intensive development.

4.2.3.2 Waste Form Solid Analytical Methods

To date most analytical development work on waste form matrices has emphasized bulk analysis. While it is important to have an accurate record of the initial waste form composition, particularly for safeguards accountibility, the changes that occur due to leaching will only be detected by microanalytical or surface sensitive techniques. Some of these techniques which are most important for characterization are:

(a) Scanning (Transmission) Electron Microscopy (STEM and SEM) - These techniques are of great importance in recognizing different phases on a micron scale. For elemental analysis by X-ray fluorescence, the transmission mode is much better. Very little work has yet been carried out on phase separated glasses of multi-phase ceramic waste forms using STEM.

(b) Scanning Auger Microscopy - This high resolution technique is also surface sensitive, so that very localized micro-regions can be analyzed for most elements. The technique can be used to study, for example, phase separated glasses, providing techniques are developed to minimize the large amount of charging which builds up on the insulating surface. Normal or non-scanning Auger spectroscopy has been used previously to analyze outer surfaces on leached simulated waste glasses.[52] However, because of the surface charging problem, only major elemental concentrations could be identified.

(c) Secondary Ion Mass Spectrometry (SIMS) - This technique uses a focused beam of light ions to remove secondary ions from the surface. A time based mass spectrum thus provides a record of the surface composition as the surface is gradually penetrated by the ion beam. A large dynamic sensitivity range allows trace, as well as major elements to be profiled. SIMS has been applied to the analysis of surface films on a simulated borosilicate waste glass.[53] This technique probably has the greatest potential use in characterizing waste form changes, particularly if a micron sized primary ion beam is used to study localized phenomena.

(d) X-ray Photoelectron Spectroscopy (XPS or ESCA) - This surface technique is also used to provide depth profiles of leached waste form surfaces. Studies of leached 76-68 glass surfaces have been recently reported.[9] Also, chemical information was obtainable from XPS studies of uranium oxide surfaces[76]. Oxidation of leached uranium glass surfaces has also been studied by XPS.[54]

(e) Autoradiography - In real waste forms or those doped with minor quantities of radionuclides, distributions of alpha, beta and gamma emitters could be separately measured using photographic films of different sensitivities. This has not yet been used extensively for the analysis of waste forms, Also of potential use is fission track analysis for the measurement of the distribution of fissile and fertile isotopes such as ^{239}Pu, ^{235}U, and ^{232}Th.

(f) Other Structural Techniques. Several other non-surface and non-microscopic structural techniques are capable of supplying additional information in characterizing waste form changes. X-ray diffraction is now used extensively in the determination of crystallization processes in waste glasses. Extended X-ray Absorption Fine Structure (EXAFS) also shows promise for determining localized chemical environments around many heavy elements in waste glasses[55]. Although not a true surface technique, reflectance infrared spectrophotometry has been used extensively by Clark[6] to sample the near-surface region (<1 μm in depth) during leaching to detect changes in the hydroxide bonded species.

A number of these techniques have much to offer in the characterization of waste forms. Several of them require some development for adaption to the non-conducting surfaces involved. Although the MCC evidently recognizes the value of such surface and structural techniques, characterization research needs to be sponsored by them and other organizations, in order to encourage DOE laboratories to study each solid waste form as matter of course during a leaching investigation.

4.2.3.3 Sampling

Although many of the prototypic waste form samples being studied at present are assumed to be homogeneous, it is very likely that any final monolithic waste forms will exhibit gross inhomogeneities, because of very slow cooling rates. Thus, waste form characterization studies of matrices cooled in this manner are desirable. An in-depth study of leaching solution behavior also is required. This arises from the as-yet unknown effects involved in maintaining very low concentrations (10^{-3}-10^{-6} ug/ml) of a number of waste form constituents in solution.

4.2.4 Test Method Review

The three main functions which leachability measurements serve are: a) quality assurance, b) comparison of different waste forms in the effectiveness of retaining radionuclides, for which "short-term" tests are often sufficient, and, c) assistance in prediction of the long-term performance of the waste form, for which "long-term" tests are a necessity.

Leach testing involves exposure of a solid sample of known composition and surface area, to a leaching medium, also of predetermined composition and temperature, for a fixed time interval. This is followed by analysis of the leachate and surface analysis of the leached waste form.

Through the years many different tests have been used or proposed by various groups within the waste management field in this country and abroad. Particularly good summaries of leach test methods are given by Mendel[21] and Flynn, et al.[40] Some of the better known tests are listed below.[56]

Table 4.1

Compilation of Waste Form Leach Tests

Organization	Salient Feature of Tests	Reference
IAEA	Periodic water replacement	Hespe 1971 (57)
ISO	Long term, periodic water replacement	ISO 5/N 38 (58)
ASTM	Closed bottle, with shaking	ANSI/ASTM C-227-73 (59)
ANS	Periodic water replacement	Anders, et al., 1979 (60)
TRU	Periodic water replacement	Johnstone 1979 (61)
DIN	Static powders/acid titration	Scholes 1952 (62)

Table 4.1 (Cont'd.)

Organization	Salient Feature of Tests	Reference
Paige	Air lift, recycle	Mendel 1973 (21)
ISO	Soxhlet - cyclic, effectively large water volume	ISO 5/N 40 (63)
LLL	Continuous flow	Coles, et al. 1979 (34)
PNL	Static, low temperature	Westsik 1978 (64)
PNL	Static, autoclave	Westsik, et al. 1978 (38)
LLL	Static single pass, low temperature, autoclave	Bradley, et al. (65)
CRNL	Continuous flow	AECL (66,67)
CUA	Buffered, frequent water replacement; stagnant, with frequent sampling of solution; continuous flow	Barkatt, et al. (42)

These tests are usually classified into two basic categories, static and dynamic. They evaluate leaching behavior at the two limiting boundary conditions with respect to flow rate of the leachant. There are also those tests which contain elements of both categories by requiring periodic replacement of the leachate. One of the most used leach tests of this type has been the IAEA test with its numerous modifications. The various leach test procedures are briefly described below.

4.2.4.1 Static Tests

These tests are most useful for comparative evaluation of waste forms. They involve leaching in a closed system where contact is maintained between the sample and the leachant for the duration of the experiment. Initially such a test would emphasize transient effects,[42] such as layer formation, surface irregularities, and rapid dissolution of fine particles, thus giving an unrealistic leach rate. In the case of glass leaching, in the absence of a buffer, the pH of the medium could rise due to the presence of alkaline leach products, thus increasing the leach rate. But finally, when concentrations of dissolved elements from the matrix can accumulate on the surface of the waste form and thus slow down the reaction rate, a "saturated" boundary condition will have been achieved. It is probable that most of the leaching in the repository will occur at conditions which approximate the "saturation" scenario. It is therefore important that such tests are run for sufficiently long periods to establish a steady-state behavior.

4.2.4.2 Replacement Tests

IAEA procedure - this is an essentially static system; however, the leachant is periodically replaced giving the test a dynamic aspect. The original procedure[57] has been modified many times in terms of operational aspects (sample sizes, leachant replacement intervals, etc.). In one form or another, this is the most widely used leach test, both in this country and abroad. Re-

placing the leachant solution is an attempt to simulate flow rate conditions in the natural situation and to accelerate the test. However, the flow rate simulation is very poor since the cyclic solution chemistry changes introduced by periodic solution exchange do not simulate expected conditions and the "acceleration" aspect of the test is impossible to quantify. Moreover, time variation has been shown to effect release rates. For example, Harvey[68] observed the apparent leach rate of glass at 100°C to increase as the leachant was changed less frequently. However, recent studies have shown that solution renewal at low temperature (25°C) does not have a significant effect on leach rates, and may be element dependent.[69,70]

Soxhlet type tests - these are dynamic tests in a closed recirculating system wherein a continual stream of leachant contacts the sample, portraying conditions of infinite detection. Two variations have been developed.

(1) The classical Soxhlet apparatus collects leachant in a reservoir below the sample which is kept at the boiling point. Water vapor from the reservoir is condensed and drips over the sample continually. A modification of this apparatus employs a reservoir to collect the distillate before it is recirculated over the sample, allowing a measure of temperature control of the leachant.[71]

(2) In the Paige apparatus,[72] an airlift recirculator is used to cycle the leachant between the reservoir and the sample.

In the first case, the leachant is always distilled water; the leach products concentrate in the reservoir. In the Paige apparatus, the leachant plus leach products are recirculated over the sample.

4.2.4.3 Continuous Tests

Continuous leaching or flow tests - these are dynamic procedures of various types. A large reservoir of leachant is used and either a one-pass circulation system employed,[34] or a multi-pass system in which case exchange columns are put in line to remove material leached from the samples.[21,73] The leachates are analyzed directly in the one pass system, whereas in the multi-pass system, the leachates are flushed from the exchange columns for analysis. The general character of these tests is similar to the Soxhlet type systems, except much larger in scale.

Most of these procedures involve a compromise between ideal simulations of natural conditions and experimental convenience. The thermally driven Soxhlet and multi-pass continuous flow procedures are of necesssity restricted to distilled and deionized water leachants, respectively, neither of which simulates natural conditions. Dynamic procedures, which involve recirculating leachates (air-lift (Paige) recirculating Soxhlet and multi-pass continuous flow procedures) simulate flow conditions more closely, but the accumulated leach products are thought to have an inhibiting effect on further leaching.[21]

The single-pass continuous flow procedure[34] appears to have the most experimental flexibility for allowing realistic simulation of a range of possible

natural conditions. Reservoir waters can be as fast or slow, as desired. Temperature, pressure, and radiation conditions could also be included in the test.

Since flow tests can be carried out under all possible flow conditions, they are considered the most useful in modeling the dependence of leaching on dilution parameters: flow rates and surface-to-volume ratios. These experiments can identify the flow conditions which characterize the most rapid rate of attack. For glass, in the absence of a buffer, this will most likely be encountered at a flow rate at which the pH of the medium is being controlled by the presence of alkaline leach products but a flow rate which is sufficiently high to prevent "saturation."

4.2.5 Materials Characterization Center Standard Leach Tests

In terms of radionuclide release, leachability is a primary concern for evaluating the performance of candidate waste forms. Although a large body of leaching data already exists, correlation of the data is very difficult due to differences of experimental procedures used in the past.

Three main uses of standard leach tests are: 1) quality assurance; 2) comparison of durability of alternative waste forms, both within a laboratory and between different laboratories. Such a test requires high analytical precision and rigorous adherence to a particular regime in which the use of the same units and standard leaching conditions such as temperature leachate composition, equivalent methods for waste-form surface area measurement, surface area to volume ratio, flow rate, etc. are necessary; 3) and most importantly, identifying and understanding the mechanisms of leaching. This is necessary for the purpose of scaling from laboratory experiments to actual repository conditions and prediction of future behavior of the waste form when exposed to various environments. These types of tests usually involve the change of one variable (temperature, pH, etc.) at a time and have less stringent procedures associated with them.

Of the various attempts that have been made to establish a standardized leach test[57,58,59,60,63] the most recent and encompassing are the five proposed Leach Tests[74,75] which are being developed by the MCC.

The basic philosophy of the MCC is to establish a small group of tests which encompass the relevant range of environmental conditions.[56] They have included most of the important features of many of the previously mentioned tests (section 4.2.3), but the one commonly used feature, namely the periodic replacement of the leachate as proposed in the IAEA, ISO, ANS, and TRU tests, has not been adopted. The reason is that time variation has been shown to affect measured release rates.[39,68]

Both, static and flow tests have been included. While all of these tests are useful for a variety of purposes, the two static tests, especially if run for only short periods of time, are most applicable to "scoping" or quick waste form comparisons and quality assurance. The third test is mainly for determining solubilities. Flow tests, especially if run for long periods, are most useful for mechanistic studies. These tests are:

MCC-1 : static, monolithic, single pass, low temperature (40°,70°,90°C)
MCC-2 : static, monolithic, single pass, high temperature (110°,150°,190°C)
MCC-3 : static, solubility, powdered samples, high temperature (110°,150°,190°C)
MCC-4 : low flow, monolithic, single pass
MCC-5 : high flow (Soxhlet), monolithic.

Of the many parameters to be evaluated, some are fixed for the comparative tests, but in other cases must be varied. All of these tests measure time dependence and the first four include variations in temperature and the use of three standard leachants: deionized water, silicate ground water, and salt brine. Site-specific leachants may be used under specific conditions. With the exception of MCC-3, which uses powdered samples, the material to be evaluated must be monolithic and its geometric surface area must be used when expressing leach rates. All tests require multi-element analyses and measurement of the pH of the leachate. Bulk chemical analysis before leaching is required and post-leach solid-state analyses such as x-ray diffraction, depth profiling, XPS, and SEM are strongly recommended for other laboratories and are actually performed by MCC on specimens after long-duration tests.

The MCC feels that although there is a scientific basis for controlling pH and Eh in some cases, this would introduce complexities to the procedures which many laboratories might not be willing to implement. However, they do state that in the long-term detailed tests and autoclave tests some type of pH and oxygen fugacity control will be required. The details of these tests have not yet been resolved.

It should be pointed out that a separate sample is used in MCC-1 and MCC-2 for each leaching period and therefore it is important that all the samples be as identical as possible.

MCC-5 most closely resembles the Soxhlet test but it differs from the original test in three ways: a monolithic sample replaces the powdered sample, an all Teflon apparatus is required as is solution analysis.

The MCC-1 static leach test,[77] the MCC-2 static high temperature leach test and supporting data have already been submitted to the MRB for approval. To this point the MRB have given these tests a probationary status.

A round-robin intercomparison test of MCC-1 has been started with about 15 organizations participating in this country and 5 in Europe. In case the agreement between the laboratories is poor, it would be difficult to know whether to ascribe the fault to problems with the leach test or the analytical procedures used to analyze the leachates. Therefore, a series of test "round-robin" solutions were sent to each participating laboratory to determine the level of agreement on the determination of trace elements. Due to budgetary restraints, not all of the laboratories have analyzed these solutions. The results from these tests should be in by May of 1981.*

*Results have been accumulated, but have not been reviewed here because of time limitations.

The MCC feels that the collection of the above mentioned tests (MCC 1-5) plus future systems tests with waste forms, barriers, and rocks present, will provide the information needed to judge conformance to criteria established by federal licensing organizations.[56]

It must be emphasized that although the tests are still in a developmental stage, the MCC has accomplished much in one year.

4.2.6 Accelerated Leach Testing

The acceleration of waste form leaching may, in principle, be achieved by changing such parameters as temperature, SA/V, composition of the leachant, flow rate, surface potential of the waste form, and radiation field.

As discussed before, an increase in temperature usually increases leach rates. However, if temperature is to be used as an acceleration parameter, it must be done with the understanding that mechanistic changes can occur and therefore an understanding of the leaching mechanisms which dominate at different temperatures is imperative. In that case, all other physiochemical variables should be kept constant, particularly solution composition. A change in temperature may change the solubilities of gases such as CO_2 and O_2 in the solution and the pH of the solution.

Adjustment of leachant composition is another potential method to accelerate waste form leaching. Such two important solution parameters are pH and oxygen content. As discussed in part 4.2.1, diffusion-controlled leaching may be accelerated by lowering solution pH, while silicate network dissolution would be accelerated by increasing the pH. Thus, pH may be used as an acceleration parameter only if the dissolution mechanism is well understood. Before adjustment in Eh is used for acceleration of waste form leaching, the effects of oxygen in the range of expected repository conditions should be known. This is particularly important during the period after repository closure when radiolysis of any water contacting the waste form will produce oxidizing species.

It appears quite possible to carry out a temperature accelerated leaching scheme based on the linear response principle outlined in Chapter 2, Section 2.4.6. However, the fact that this type of approach has not yet been applied to any waste form leaching system suggests that there is not yet enough exactitude in leach measurements to allow the continuity of mechanistic behavior to be verified over a given temperature range. Moreover, there is no indication that leaching at a higher temperature can necessarily even be regarded as a "worst case" situation in qualitative terms. Therefore, the use of temperature accelerated leaching should be curtailed until mechanistic continuity can be proven for the temperature range in question.

4.2.7 Extrapolation

Long-term leaching of the waste form has been modelled mathematically by several groups.[35,78,79] In the case of glasses, most agree that diffusion from the waste form would be rate-limited by the surface layer, which will probably form through precipitation processes. This means that the mass transferred will vary in some way with the square root of time. However, the choice of the actual equation, can change the long term result by several orders of

magnitude. There is, thus, no way that such models can be relied upon until much longer-term experimental data has been completed and its fit to various models assessed.

4.2.8 Conclusions and Recommendations

To achieve a waste form with leaching characteristics compatible with the proposed NRC release criteria, the testing program might be expected to include the following major tasks:

(1) Agreement on specific leach test procedures to be used by program participants and development of analytical procedures with enough range and sensitivity to support the program.

(2) Use of the above procedures to develop an understanding of leaching mechanisms and to develop models for long-term dissolution.

(3) Development of tests on full-scale waste forms which demonstrate a capability for containing radioactivity release within predetermined fractional limits.

Since its formation 18 months ago, the Materials Characterization Center has specifically addressed the first of these tasks and has made substantial progress in establishing greater confidence in leach testing as the major method of evaluation for the waste form. In the past, comparison of leach results between different research groups has been difficult, because of inconsistent test methodologies or the use of analytical chemistry procedures with inadequate or barely adequate sensitivity. The MCC has commendably endeavored to reduce confusion by developing a series of well-documented single-component leaching tests, covering most conceivable geologic leaching situations, yet flexible enough to be used by the more fundamental leaching researchers. The MCC has also greatly improved communication within the leaching community through the sponsorship of workshops and round-robin intercomparisons dealing with different aspects of waste form leaching. The recent improvement in agreement of leach data from different DOE laboratories must be partially attributed to efforts of the MCC.

As the quality of the standard test data improves, it is hoped that the MCC will place increased emphasis on the meaning of the present data and on methods to improve our knowledge of the basic release mechanisms. The MCC has in fact indicated a desire to move in this direction, but funding for such work is still uncertain and is dependent on other decisions taken by the lead laboratory (SRL).

The importance of emphasizing such fundamental mechanistic studies of waste form leaching has been referred to several times in this chapter. We are nevertheless concerned that the emphasis in leach testing will, in fact, continue to be placed on the comparison of specific radionuclide release rates, after relatively brief (<5 years) exposures to leaching conditions. However, any long-term prediction of release behavior will require an understanding of the principal migration and dissolution mechanisms of a number of radionuclide isotopes to be incorporated in the waste form with the emphasis on radionuclides which will still be present after the thousand year containment.

This task group thus considers it more important that the release mechanism for several chemically different radionuclides in a given waste form be explained in thorough scientific terms, than, it necessarily have the lowest achievable experimental leach rates for a given test period. Thus, the extent to which a waste form can be well-characterized mechanistically should have considerable bearing on its admissibility as a waste form.

At this moment, certain aspects of the leaching behavior of spent fuel appear to be better understood than that of any other waste form. The release of a large number of nuclides has been monitered over a several year period. Results from research groups using different types of fuel are in good agreement. Electrochemical studies of the dissolution mechanisms of the matrix are well advanced. While we recognize that spent fuel has some fortuitious testing characteristics (e.g. an electrically conducting matrix which permits elecrochemical studies to be performed), it serves, none the less, as a good example of the depth of testing which should be required for other waste forms.

Although mechanistic studies for glass waste forms appear to be still in the initial stages in many laboratories, those for multi-phase ceramic waste forms are much further behind. Mechanistic characterization of these ceramic waste forms, however, is even more important than for glasses, since the variety of chemical products which can form from multi-phase systems is far greater.

The MCC has, for the first time, begun to put emphasis on characterization of the total system during a leaching experiment. We believe that surface and microanalysis of the waste form is as important an aspect as solution analysis itself, in reaching an understanding of the leaching mechanisms involved. Much research needs to be initiated in the use of promising surface analysis techniques, such as Secondary Ion Mass Spectrometry, applied to waste form analysis. In addition, solution analytical methods need to be developed to allow detection of concentrations as low as 10^{-6} µg/ml in ambient temperature leaching solutions. High Pressure Liquid Chromatography (HPLC) appears to be a particularly promising technique to be developed for this purpose, alongside neutron activation analysis.

The question of whether static or dynamic leaching conditions are more suitable for evaluating long term leaching has been argued for many years. Recently, opinion in the leaching community seems to be favoring the use of static conditions, because the measured groundwater velocities in test sites are usually so low as to be virtually static. By contrast, our opinion favors more research on higher flow rate conditions because: (a) high flow conditions present the maximum risk as far as radionuclide release, (b) high flow conditions present a much more constant solution environment thus facilitating mechanistic studies on the waste form, and (c) even if high ground water flow rates are not present in the environment, similiar chemical effects may likely be created by the presence of highly absorbant geological materials such as backfills.

It is recognized that continuous flow leaching studies are much more technically demanding than the present static leach tests. This group feels that there is a clear need for at least one highly-regulated and instrumented test loop in the DOE program, where long-term leaching studies could be carried out under well-controlled flow, Eh, pH and temperature conditions and where the solutions and waste forms could be analyzed by state-of-the-art techniques.

This type of program would probably best be coordinated at a center where studies of the thermodynamic and kinetic stabilities of waste form type materials are currently underway. The objective of this program would be to develop mechanistic information about long-term waste form leaching, particularly under high flow conditions, rather than comparative testing of alternative waste forms.

Research work is certainly necessary to understand the relationship between surface area measurements by different techniques. While BET measurements are apparantly applicable to all types of waste forms, there is some doubt that the area being measured corresponds to that actually in contact with the leachant.

The proper sampling of waste forms is likely to be a continuing problem, particularly as process scale-up proceeds. In the case of glasses, segregation in the slowly cooled monolith could result in waste forms with either excessive or deficient quantities of radionuclides on the surface and this surface must be sampled properly for tests evaluating conformance with release criteria. The size of the final waste form may have to take the sampling difficulties into account.

The task of relating leach rate data to some fractional release criteria has not yet been addressed by any group. A recent communication[80] suggests that fractional release should vary linearly with surface/volume ratio (S/V) of the waste form. Assuming the surface area of the monolith is not increased significantly by cracking, and segregation (see above) is minor, it should be relatively straightforward to determine fractional release for any size of monolith, using the leach rate data. This approach should be tested experimentally, comparing the fractional release of radiouclides from different sizes and shapes of actual waste form monoliths with the release data calculated from a leach rate of small standard leach test of the same material. The effect of thermally - or mechanically - induced cracking of the monolith exterior should also be determined.

Although there has been some interest shown by the MCC in evaluating fractional release rates for waste form materials, there appears to be no financial support for their undertaking of such a program. Partly for this reason, we recommend that the NRC consider sponsoring studies of the effects of scale-up on fractional release rates. Even if such work were to be undertaken by the MCC, independent confirmatory data on fractional release is of prime importance to the NRC postion in 10CFR60.

4.3 Mechanical Property Tests

4.3.1 Introduction

Although mechanical failure of the waste form is much less likely to cause release of radioactivity than is chemical leaching, there are certain "worst case" scenarios in which failure of the waste form could lead to release of particulates or an increase in surface/volume ratio for enhanced leaching. The former situation is most likely to occur during fabrication or transport to the repository, while the latter will occur during repository-induced stresses. Several types of generic mechanical damage are expected to take place in these circumstances. Given below is an evaluation of mechanical testing methods relevant to various waste form types.

4.3.2 Tensile and Compression Testing

4.3.2.1 Test Methods

The method of measuring the compressive strength of ceramic materials is standardized in ASTM C773.[81] This method is equally applicable to a glassy waste form. The test specimen should be a right cylinder. Any kind of controlled-speed compression machine may be used to load the specimen. For specimen alignment and the avoidance of any accidental perturbation such as stress concentration at individual contact points, auxiliary accessories are used, including spherical bearing blocks and contact blocks (pad materials).

Glass and ceramic materials exhibit very high compressive strength when compared to their tensile strength. An order of magnitude difference between these two strengths has often been reported. This could often lead to frequent fracture of a waste form by tensile stresses, not only by the application of a tensile force, but also by the development of tensile stresses at a certain portion of waste form during general compression.

As a generic method, the modulus of rupture is considered a valid measure of the tensile strength. The standard method of flexural strength measurement is specified in ASTM C158.[82] With rectangular specimens, three- or four-point bending is often used in a controlled-speed compression machine. The obtained maximum bending moment is correlated to tensile strength. While the flexure test is generally applicable to brittle solids as well as ductile solids, the recent MCC tensile test[83] is a more adequate design for the brittle solids, with better reproducibility and accuracy. The MCC proposal is based on an earlier study of diametrical compression testing developed at Sandia.[84] Figure 4.2 shows a schematic of the MCC-11 tensile strength test. The load is applied diametrically, with the flat surfaces of the specimen being parallel to the applied load. As the moving bearing block applies an increasing load, the resultant stress eventually increases to the fracture strength of the material and the specimen splits along the vertical diameter.

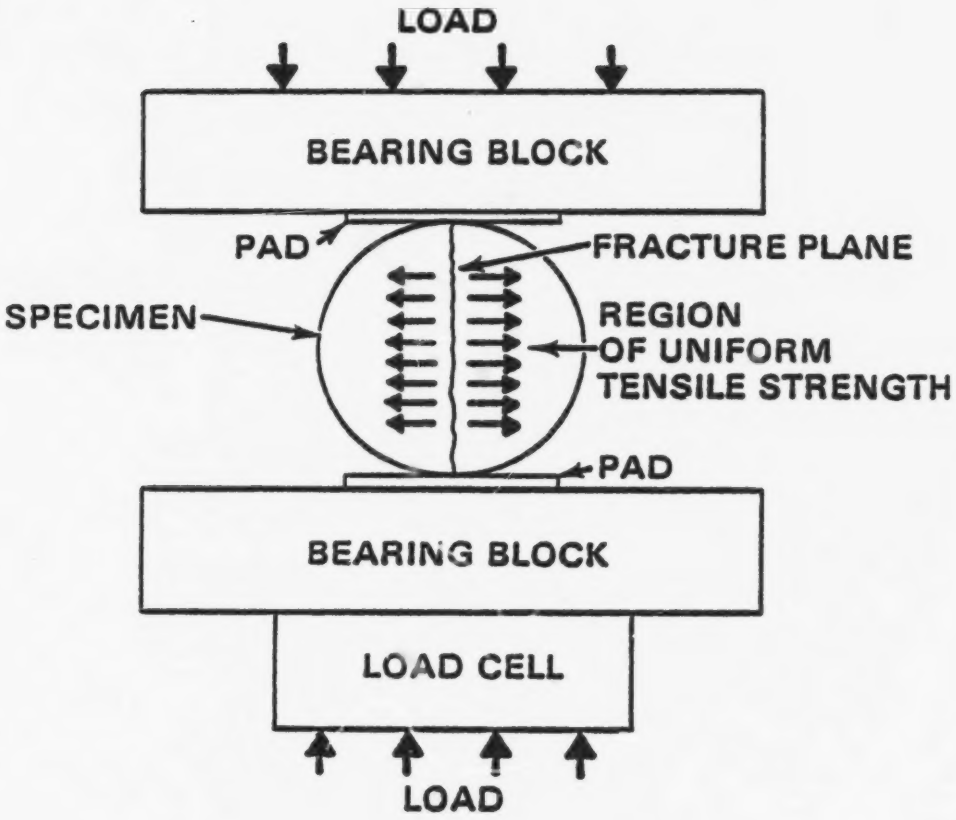

Figure 4.2. MCC tensile strength test.

4.3.2.2 Variables

(a) Rate of Stressing: Testing speed itself will not significantly affect the stength of brittle solids within the bond specified. A slow testing speed is commonly used because the test is intended to derive results applicable to static stresses.

(b) Surface Conditions: To avoid surface stress concentration at local inhomogeneities, grinding and lapping of the sample are desirable. In MCC-11, grinding with 200-grit SiC or tool-post grinding on a lathe using 60-grit Al_2O_3 is recommended.

(c) Bearing Blocks and Padding Materials: In principle, these two materials should not affect the fracture strength. For this purpose, a certain strength and softness are required. For example, in MCC-11, Rc60 hardness, or greater, is required for bearing blocks, while pad materials must be hard enough that they cannot be penetrated by the specimen but soft enough to distribute the load over a small area. Balsa wood, Al and Cu foil are recommended for this purpose.

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(d) Heat Treatment: For crystalline material, heat treatment affects the grain growth, while stress relaxation takes place in glassy materials as a result of heat. A well-annealed specimen is recommended initially. If a specific initial microstructure is required by heat treatment, the initial heat treatment should be specified.

(e) Sample Number: For reproducibility, a minimum of five to ten specimens are required in most of the above cases.

(f) Environmental Effect: Most high-level waste forms are not porous and are not susceptible to direct environmental effects, e.g., those due to temperature and humidity, as observed in cement encapsulated low-level wastes.

4.3.3 Impact Testing

4.3.3.1 Test Methods

Basically, two types of tests are available: drop weight and free fall. In the former, a weight is dropped on a specimen placed between two hardened steel plates in a sealed chamber. Earlier development is standardized in ASTM[85,86] for the test of generic materials. For waste form materials, ANL[87-89] developed this type of test with the attachment of a bellows-controlled particle collection system to use after the fracture of the sample. More sophisticated tests are performed by monitoring the time vs. force characteristics with the attachment of a load cell. Bandypadhyay of ANL[90] and MCC-10[91] use this sophisticated test. An illustration of the MCC test is shown in Figure 4.3. The attached load cell can give the correct impact energy input as a function of time. Information on the secondary crushing is obtained in this way. DYNATUP is a commercially available machine of this type.

In the free-fall test, less damage occurs if the sample is dropped onto a surface. ANL[87-89,92] uses this method for comparison with the drop-weight test, while earlier PNL[93] free-fall tests of the waste package have been for the assessment of the quantity of respirable glass fines. A free-fall specimen yields a configuration resembling a truncated cone, while impact delivered by the drop-weight device produces a barrel-shaped specimen.

The specimen is in the shape of a cylinder[89] (3.8 cm OD and 6.4 cm length or smaller). The load can be applied either diametrically or axially. The workshop of MCC[94] suggested that the axial test is more desirable because the more uniform stress distribution allows an estimate of absorbed energy.

The subsequent size analysis of particles after impact is another major job because of the risk of inhalation of dust particles and the increased amount leached with the increased surface area. Bigger particles are

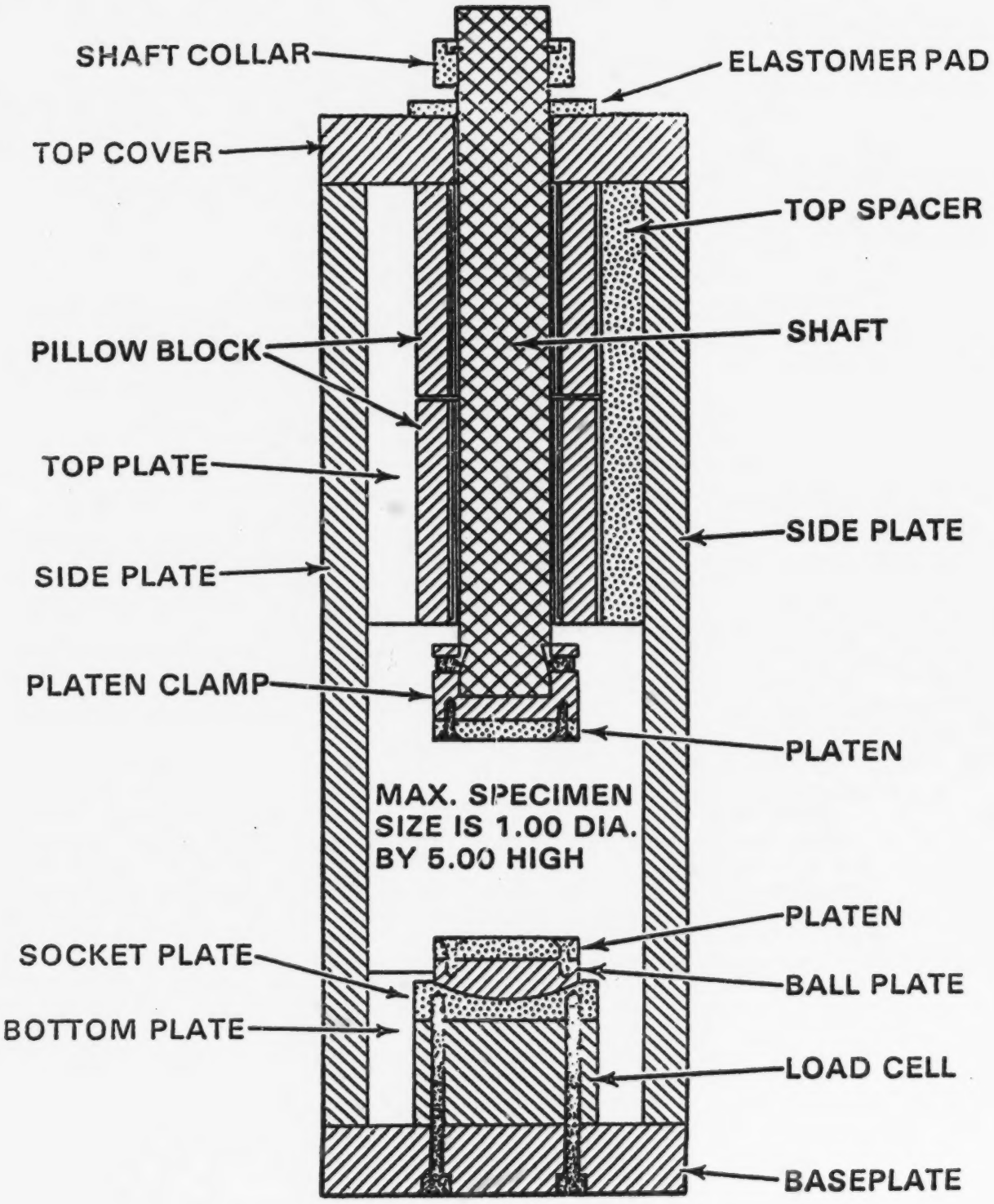

Figure 4.3. Drop weight - impact test proposed in MCC-10.

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measured by a microscopic technique, while smaller particles are measured by BET gas adsorption, a Coulter counter, sieving or sedimentation. The results obtained by these different methods are not consistent, and effort is being given to explaining this inconsistency.

4.3.3.2 Variables

(a) Drop Height: In the drop-weight and the free-fall test, the drop height is one of the factors determining the total energy input. In the MCC test, a height of 50 cm is used, while 7.6 m has been used for the bench-scale test of the PNL package.

(b) Drop Weight: The recommended drop weight is dependent on the materials of the specimen and the drop height. For a desirable breakage, the weight should be neither too heavy nor too light. In the MCC test, the maximum is known to be 760 kg.

(c) Surface Finish and End Effect: If substantially different surface finishes are used, the data obtained should be accompanied by a footnote specifying the finished use, since the local inhomogeneity may change the breakage pattern of the sample. In particular, the end effect is influenced by the surface inhomogeneity. To reduce the end effect, the increased ratio of axis-to-radius is used.

(d) Environment: As in the tensile test, no direct effect of environmental variables such as temperature has been reported.

(e) Heat Treatment: Heat treatment changes not only the fracture pattern but also the absolute quantity of the fractured particles. For instance, the tempered specimens showed a fracture thereshold greater than that of the annealed specimens by a factor of about 10[93] for the same impact. For this reason, heat treatment conditions should be specified before testing.

4.3.4 Fracture Mechanics Testing

The study of fracture mechanics is basic to the prediction of the structural disintegration of the waste form by delayed failure over geologic time. For example, the static fatigue of glass has been studied very systematically through fracture mechanics. However, little attention has been given to evaluating various generic methods of fracture mechanics for nuclear waste form evaluation, and consequently no literature is available. In the generic tests, the Double Cantilever Beam Technique, the Double Torsion Technique, and the Notched Bend Test are used for the quantitative assessment of crack growth rate as a function of a given stress intensity.[95] Also in this way, the critical stress intensity factor is obtained. For qualitative assessment, the indentation technique is used. The details of the design of samples are tabulated in Ref. 96.

4.3.5 Conclusions and Recommendations

Development of tests for assurance of waste form mechanical properties is well underway. However, emphasis has been given to impact and tensile tests to cover accidents which might occur before placement in a repository. This group believes that it is more important to develop fracture mechanics tests for long-term repository stresses. It is recognized that this task will be more difficult than the present one, since little is known about how the failure mechanism may change as a result of increased stress or energy input. Some generic fracture mechanical test methods have been suggested for such studies.

In waste form characterization, tensile tests and impact fracture tests have been standardized by the MCC. The radial tension test is the most desirable, while the axial test is recommended for the impact test. In the impact test, it is recommended that the input energy be monitored by a load cell attachment and that the particle size be measured by the BET method for consistency with the metallographic method and sieve analysis. The acceleration method of mechanical testing has used a stress or energy input. For risk analysis during in-plant handling and storage, and during off site transportation of waste package, this type of testing is sufficient for the selection and design of proper waste forms.

Special standardized tests will be required for multibarrier waste forms. Test methods for brittle and ductile solids will be quite different, and a waste form containing both (e.g., glass in a metal matrix) must be mechanically tested under a specialized set of conditions.

4.4 Radiation Effects in Waste Form Testing

4.4.1 Introduction

In this section, we first describe the radiation conditions expected to exist in waste forms, and the general effects which may result in the waste package components. The potential impact of these effects on leach, mechanical and other testing is then discussed. At this point, certain preliminary conclusions concerning testing and interpretation can be drawn, and several outstanding questions defined. These are presented in the last section.

4.4.2 Radiation Environment in the Waste Form

Within the waste package, the radiation environment will vary with both space and time. Characteristic features of the radiation environment are shown in Table 4.2. Fission fragments in high level waste forms will decay primarily by beta-emission, producing energetic electrons and gamma rays. These decays will account for most of the heat and radioactivity generated initially within the waste form.[97] Substantial gamma ray, energetic electron and thermal fluxes within the waste package will largely be confined to the first several hundred years after burial. Energetic electrons

generated in fission fragment decay will be largely restricted to the immediate vicinity of the waste form -gamma rays are vastly more penetrating.

Unlike the situation for fission fragments, the important decay mode for TRU elements is alpha particle emission. While other radiations are produced in the TRU decay chains, the emitted alpha particle and recoil nucleus will produce most of the radiation damage. These particles interact quite strongly with matter, and the primary damage ranges are extremely small.

Both alpha and beta decay result in atomic transmutations. The decay products can be quite different chemically from the parent radionuclide. For example, when ^{90}Sr is transmuted to ^{90}Zr by successive beta decays, the valence increases by + 2 and the ionic radius decreases by 38 percent. Such changes might affect the stability of the radionuclide host phase.

Alpha decay in TRU elements is an inherently long lived process, typically involving a number of intermediate species. Alpha decays will continue to accumulate in waste forms for many thousands of years after the thermal and beta/gamma fluxes from fission fragments have decayed. Substantially different time scales should be used when considering the effects of beta/gamma irradiation and those of alpha decays.

4.4.3 Mechanistic Considerations

Gamma rays lose energy in matter mainly by producing energetic electrons. Occasionally, these may cause atomic displacements by elastic collision. Far more frequently, however, the energetic electrons displace other electrons - chemical bonds may be ruptured, valence states modified, etc. These processes can be viewed as radiochemical or ionization effects fundamentally involving electronic charge transfer.

Energetic electrons resulting directly from beta decay interact with matter in the same way as the Compton or photoelectrons due to gamma irradiation. Again, for most solids, the principal effect is ionization; Hall, et al.[98] have estimated that in a waste glass only about one atom is displaced by elastic collisions for every eight beta particles emitted.

Atomic displacements are readily provided by "knock-on" elastic collisions in internal alpha decay. The heavy recoil nucleus in particular can displace roughly 2000 atoms.[104] The number of atomic displacements produced by elastic collisons in typical waste forms by internal alpha decay has been estimated to be at least 100 times greater than due to other mechanisms. Helium is also formed when alpha particles are stopped in matter. When large numbers of stable displaced atoms are produced, the bulk physical properties of materials are altered.† (Table 4.2 and Figures 4.4 and 4.5)

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†When atomic displacements are produced by elastic collisions, the process is termed "knock-on" or displacement damage. In some cases displaced atoms may be produced by ionization; this is termed "ionization damage" or internal radiolysis.

Table 4.2

Radiation Environment for the Waste Form

Radiation	Range (mm)	Dose After 10^6 years	Time Scale+	Effects
Alpha recoil	10^{-5}	10^{19}/cm^3(c) 10^{17}/cm^3(d)	~10% in 1000 years	o ~2000 knock-on atomic displacements per decay
Alpha particle	2.5×20^{-2}	10^{19}/cm^3(c)	~10% in 1000 years	o ~150 knock-on atomic displacements per decay o ionization 10^{19}/g = 8×10^{11} rad (bulk) o helium formation
Beta particle	1	2×10^{20}/cm^3(c)	>90% in 1000 years	o ~0.13 knock-on atomic displacements per decay o ionization (10^{11}-10^{12} rad) o charge transfer o heating
Gamma ray	10^{-3}	10^{11}-10^{12} rad	>90% in 1000 years	o ionization o charge transfer o heating
Fission fragment	2×10^{-2}	2×10^{13}/cm^3(c)	>90% in 10 years	o ~10 knock-on atomic displacements per decay o ionization (97.5%) 10^{13}/g = 6×10^7 rad (bulk)

c = commercial HLW
d = defense HLW
+ = relative to the million-year dose

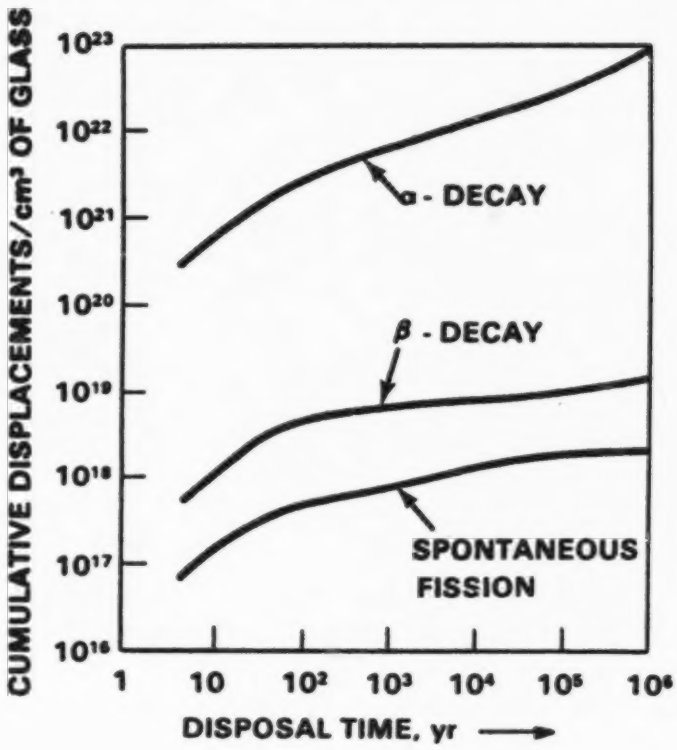

Figure 4.4. Cumulative atomic displacements calculated for knock-on processes in commercial HLW solid. From Roberts, et. al.(106)

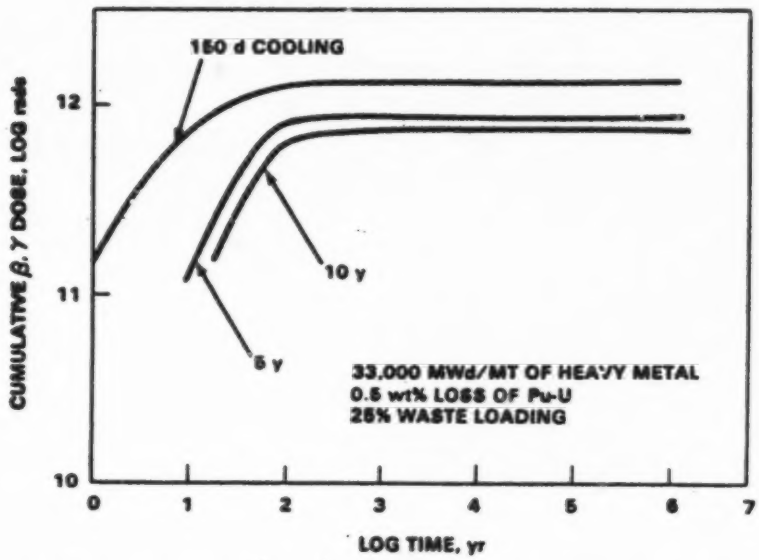

Figure 4.5. Cumulative ionization dose from beta and gamma radiation in commercial HLW solid. From Roberts, et. al.(114)

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The mechanisms described above can, in principle, produce a number of effects which have a direct bearing on test procedures and development:

- Atomic displacement can cause compaction of glasses, and metamictization of minerals, possibly accompanied by swelling and gas buildup.[100-102] Such effects may modify leach rates; a number of evaluations have been carried out for specific waste form candidates.[30,32,97,98,103-111] The time scale for displacement damage due to alpha decays is long enough so that laboratory evaluation commonly involves drastically accelerated testing; displacement doses which would accumulate over thousands of years in the repository environment are administered in a few years. If radionuclides are nonuniformly distributed on a scale which is large compared with the range of a recoil nucleus, spatial fluctuations in the alpha-recoil dose will occur. Under these conditions, differential effects such as local swelling could conceivably affect the leach resistance of the waste form.[32,112,113]

- Internal ionization within the waste form is commonly expected to provide only a relatively small number of atomic displacements in comparison to the alpha recoil damage.[115],(Figure 4.4) However, there is increasing evidence to suggest that ionizing radiation at repository doses can produce non-negligible atomic displacements and structural damage in some oxides of interest as candidate waste forms.[116-120]

- Depending upon the mechanism, structural radiation damage in waste form radionuclide hosts could exhibit a non-monotonic temperature dependence with a clearly defined maximum.[121,122] On theoretical grounds, one also expects that, at fixed temperature, the damage formation efficiency could show a maximum at some critical dose rate.[123]

- For ionizing radiation in the waste form, of perhaps equal importance are effects associated with internal charge transfer. If a glass or ceramic waste form changes color under irradiation, it is likely that changes in oxidation states have taken place.[124] There are also situations in which modified atomic species or defects exist in substantial numbers only during irradiation.[125] In others, however, atoms rendered mobile by irradiation may remain mobile after the irradiation has ended.[126]

- Ionizing radiation emitted from the waste form may alter environmental conditions in the repository. Specifically, the chemical nature of leachants may be modified by gamma, beta, or alpha-radiolysis.[127,128] Steady state concentrations of radiolysis products may depend on the type of radiation and radiation dose rate.[127,129]

4.4.4 Radiation Effects in Leach Testing

Tests have been carried out to determine the effects of displacement damage, ionization damage and radiolysis effects on leaching behavior. The various techniques are described below. One of two methods is generally employed: the sample is either leached while it is being irradiated, or sequentially ir-

radiated then leached. All tests of which we are aware are either of the static or Soxhlet type.

4.4.4.1 Displacement Damage Studies

Methods which have been employed to simulate the displacement damage due to internal alpha decay in waste forms include:

- Doping with short-lived alpha-emitters such as $^{244,242}Cm$, ^{238}Pu, and ^{241}Am. (30,97,98,103-106)
- Internal fission.(130)
- Neutron bombardment.(32,99,106,107,113)
- Heavy ion bombardment (implantation).(99,108-111)

The method of internal doping with actinide alpha-emitters has the advantage that alpha particles and recoil nuclei are generated simultaneously, as in the actual waste form. A few years may be necessary to obtain dose levels in the range of 10^{18} /g. The virtues of a reliable rapid screening procedure are apparent. The external bombardment and internal fission techniques referred to above have been examined largely from the viewpoint of developing such a procedure; each, however, has its drawbacks, as we shall describe.

For samples which have been internally doped, the leach rate is measured as the radiation dose builds up: the sample may be either continuously or intermittantly contacted with the leachant.(30,103) For ion-bombarded samples, only a thin surface layer is studied; consequently, differential depth profiling of irradiated and unirradiated zones is used to study chemical etching in leachant solutions. In certain cases, the actinide doping and bombardment techniques are said to give significantly different results.(108-111)

4.4.4.2 Ionization Damage Studies

Only a few tests have been designed to evaluate the effects of ionizing radiation on leach resistance. McVay and co-workers,(43) and more recently, Bibler,et al.(131) have carried out static leach tests on samples during gamma irradiation. In each experiment, the sample is contacted with the leachant and both are then gamma irradiated in noble metal crucibles. Leaching is measured by periodic solution analysis. In these experiments, radiation effects in both the sample and the leachant are simultaneously observed. A few experiments(43,98,114) have been carried out in which waste glasses have been gamma or electron irradiated and then exposed to leachants.

4.4.4.3 Transmutation Effects

The effects of internal transmutation due to beta decay may be the most difficult to simulate for test purposes. It is important, in view of the com-

plexities which accurate simulation would entail, that some initial screening be undertaken promptly. Recently, workers at PNL[132] have reported initial results in which neutron capture has been employed to accelerate the Cs Ba transmutation. Several waste form materials containing ^{133}Cs were neutron irradiated, converting about 12% of the ^{133}Cs to ^{134}Cs, which decays to ^{134}Ba with a 2 year half life. Following irradiation, samples were annealed to remove neutron damage. The samples are held at ambient temperatures as the transmutations build up. Periodically, the leach rate is monitored in 7-day static tests at 90°C.

4.4.4.4 Radiolysis of Leachants

The possible effects of leachant radiolysis have received some emphasis in leach testing. Recently, studies have been carried out at SRL, investigating alpha and beta radiolysis effects, as well as the leaching under gamma radiation referred to earlier.[131] The alpha radiolysis measurements were carried out using a glass test sample doped with ^{244}Cm. The beta-radiolysis was produced by ^{90}Sr decay in a sample containing actual SRP waste. In this study, and in earlier work at PNL[43], effects of gamma radiolysis products on leachant pH were emphasized.

Calculations of radiolysis product concentrations have been carried out for water[129] and for repository conditions[128]. One may inquire whether leaching under gamma irradiation could be simulated by using leachants containing simulated radiolysis products. The PNL authors have attempted such a simulation. They find that for eight of the nine elements tested, the five-day leach rates in a nitric acid solution without irradiation are similar to those measured for five-day leaching in deionized water during irradiation (in the presence of air). In these experiments, and those at SRL, it appears that the major effect on leach rates may be due to an irradiation induced decrease of leachant pH. It is not yet clear whether this mechanism can account for all the observed changes.

4.4.5 Radiation Effects on Structural Stability and Mechanical Property Tests.

Displacement damage and, in some cases, ionization damage can change the structural and mechanical properties of waste form materials. Structural effects include loss of crystallinity (metamictization) and volume changes. Mechanical effects include microfracture.

4.4.5.1 Displacement Damage Studies

Methods which have been used to simulate displacements due to internal alpha decay have been outlined in section 4.4.4.1. In studying displacement damage effects on mechanical properties, or microstructure, the sample is first irradiated and then characterized. Most commonly, these characterizations involve optical microscopy, x-ray diffraction (XRD) measurements, and determination of density changes. Sample surface may also be examined by SEM and, where doped samples are used, by alpha autoradiography. Commonly, the

magnitude of the irradiation induced changes in parameters such as density, x-ray lattice constant, x-ray peak height, etc., is plotted vs. irradiation dose. These curves commonly show saturation behavior.[114] For glasses either volume expansion or compaction may be observed.

It would be quite useful to compare curves such as those described above which are produced by different irradiation techniques. Unfortunately, a detailed comparison is not yet possible for most materials.[133] For techniques such as heavy-ion bombardment, where the particle range is small, special techniques such as TEM are employed.[134]

4.4.5.2 Ionization Damage Studies

Recently Shelby[118] has completed a study of the effect of gamma radiation on the density, refractive index, thermal expansion and helium permeability of a number of commercial borosilicate glasses. Volume compactions approaching 1% were observed at 10^{10} rads, a radiation dose which is at least an order of magnitude lower than that anticipated in certain HLW glass. These data suggest that ionizing radiation may produce structural changes in HLW glass which are at least as significant as those due to internal alpha decay. This point should receive increased emphasis in testing.

Historically, the possibility of radiation damage has been viewed as a drawback to electron microscopy of insulators. More recently, as emphasized by Hobbs[120], the electron microscope has been profitably employed to produce and simultaneously observe radiation damage in insulators. The instrument provides structural information on a very fine scale, although limited to surfaces (SEM) or extremely thin foils (TEM). By studying the dependence of damage formation on electron energy, one may demonstrate the existence of ionization damage (radiolysis) effects in materials such as quartz, some silicates and carbonates.[119]

It should be pointed out that the quantitative correspondence between electron microscope irradiations and electron bombardment in large accelerators may not always be clear. For example, Hall, et al. have reported bubble formation (evidently not due to helium) for prototype waste glass irradiated in the TEM. This effect was not observed under Van de Graff electron irradiation at presumably equivalent doses.[98]

4.4.5.3 Alpha Particle Effects

(a) Several crystal structures have been irradiated at room temperature with alpha particles in order to simulate the alpha particle flux incident on the nonactinide-containing phases in nuclear waste solids.[132] The relative changes in lattice parameters were measured as a function of alpha dose by x-ray diffraction techniques. The observed damage ingrowth follows the same exponential dose dependence as observed in alpha-recoil damage. The data show that nonactinide-containing phases can undergo significant lattice expansions as a result of alpha bombardment from adjacent actinide host phases.

(b) Helium is formed by electron capture when alpha particles are stopped in matter. The consequences of this effect have been considered by a number of authors.[98,103,105,136] In crystalline materials, helium bubbles have been observed to form along grain boundaries, affecting mechanical properties.[100] The amount of helium produced in the waste form can be estimated from information such as that in Table 4.3. Were this helium released, it could pressurize the container. This can be avoided by providing a suitable expansion volume in the container, or by retention of the helium within the radionuclide host.

Helium diffusion rates in glass depend strongly on temperature and are apparently are decreased as radiation damage builds up.[135,136] The available evidence suggests that helium largely remains in the glass under the accelerated testing conditions where radiation effects on swelling and leach rates were studied. These experiments gave no evidence of significant helium related effects on the mechanical properties of the glasses.

In some experiments, involving external alpha bombardment or diffusion at elevated temperatures, helium bubbles have been observed. Under SEM examinations, bubbles or blisters have been found in glasses after internal alpha decay.[110] These are thought to be helium bubbles promoted by beam heating in the SEM. (However, see section 4.4.5.2).

4.4.5.4 Transmutation Effects (Mechanical/Structural)

The only direct measurements of which we are aware are those described in section 4.4.4.3. In these studies, density and lattice parameters are being monitored as the Cs Ba transmutations continue. Activity levels and transmutation densities are low compared to those anticipated in commercial HLW.

4.4.5.5 Differential Stresses and Microfracture

In certain materials fairly substantial (> 1%) volume changes may occur under irradiation. These volume changes may produce stresses in the environment of the waste form.[137] Also, there are at least three ways in which local stresses may be produced within the waste form itself.

I. A spatially inhomogeneous radiation dose is administered to a homogeneous material.

II. A spatially homogeneous radiation dose is administered to an inhomogeneous material.

III. A spatially inhomogeneous radiation dose is administered to a spatially inhomogeneous material.

With respect to alpha-recoil dose, SYNROC would fall in Case III. On the other hand, for beta-gamma dose, SYNROC would more nearly represent Case II, if the size of individual grains is small compared with the range 1 mm.

As pointed out by Martin[138] Case II behavior could occur if either the formation or relaxation of radiation damage is temperature dependent, and the material finds itself in a thermal gradient. Case II behavior might apply to homogeneous glassy systems during the first 1000 years after emplacement.

Single phase studies do not assess behavior under Case II or Case III conditions. In a notable experiment, Weber, et al. have studied the effect of devitrification on the radiation stability of curium-doped 77-260 glasses; curium-rich[104] phases tended to precipitate from the residual glass. Both swelling and the formation of surface microcracks were observed due to the differential expansion of the devitrified apatite phase with respect to the residual glass. It is particularly interesting that the glass appeared to practically retain its leach resistance.

Recently, neutron irradiation damage measurements have been reported for synthetic barium hollandite, perovskite and undoped SYNROC B.[32,101,113] Swelling and microcracking was observed in all cases. The collision mean free path for neutrons in these materials is typically several centimeters, resulting in a spatially homogeneous irradiation dose. Consequently, neutron irradiation cannot hope to reflect the local inhomogeneties in radiation damage which may occur in SYNROC waste forms. In present terms, the experiment approximates Case II conditions, while Case III behavior is expected in the actual waste form.

4.4.6 Stored Energy Measurements

Historically, stored energy has been of practical interest in radiation effects studies because of the possibility that its catastrophic release might damage critical components. It is now generally agreed that this will not be a problem in waste glass.[106] More recently, stored energy has become a useful parameter for intercomparison of radiation effects.[99]

Stored energy measurements carried out on waste glasses indicate a remarkable degree of similarity. Stored energy shows saturation behavior at an internal alpha dose near 10^{18} alphas per gram for a wide variety of materials. The saturation behavior is also implicit under neutron irradiation, heavy ion bombardment and internal fission. These latter irradiations are conducted at vastly different radiation dose rates than the internal alpha decay; however, the saturation behavior seems to persist and, when the radiation doses are normalized to estimated DPA, saturation commonly begins at about 0.1 DPA. It is at about this dose, which we take as equivalent to 10^{18} /g, that saturation behavior in the radiation induced swelling is also observed. The similarity of stored energy and swelling data obtained with different dose rates and varieties of radiation suggests that it is the number of displaced atoms and not the radiation dose rate which is a determining factor in the damage formation.[99] This result supports the validity of accelerated testing with doped samples. These speculative arguments, however, require confirmation.

4.4.7 Radiolytic Gas Generation Tests

In certain inorganic materials, gases may be generated by the radiation-induced decomposition of incorporated molecules or molecular ions. The process is sometimes viewed as similar to solution radiolysis. Waste forms incorporating water such as concrete may be particularly susceptible to radiolysis, high fired ceramics are less affected.

Radiolytic gas generation from concretes has been measured in several laboratories[141,142]. The technique involves monitoring the evolution of gas pressure as the sample is irradiated in a closed vessel. The collected gases may then be analyzed to determine the decomposition products. The yields may depend on the type of radiation (or linear energy transfer); gamma irradiation cannot in general be used to determine susceptibility to alpha-radiolysis. These testing techniques should be applicable to other materials as long as the test insures that generated gases escape from the solid (in a realistic manner).

4.4.8 Charge Buildup

Insulators may aquire an electrical charge under irradiation, either when energetic charged particles are stopped in the material, or when electrons or ions are ejected by scattering processes. Gamma rays or x-rays can cause such charging; under certain conditions the stored charge can be released as a Lichtenberg discharge or result in fracture under slight shock.[143] We do not anticipate that charge buildup and attendant fracture is particularly likely to occur under repository conditions, but some sort of confirmatory assessment should be undertaken. We are not aware of any standard test procedures.

4.4.9 Development of Standard Tests by DOE

The development of standard radiation test procedures for the waste form presents two challenges. First, one must decide how best to simulate the various radiation effects anticipated in the repository. Having done so, a standard method of evaluating these effects must be specified. Development of standard waste form tests for the effects of radiation is still at an early stage.

4.4.9.1 General Activities

A few workshops[119,144] and panels[115,145] have met over the past few years to consider radiation effects in radioactive waste forms and other waste package materials. Several reviews have also recently appeared[137,146-148]. In addition, there is a steady emergence of test results in the HLW waste management literature. For example, at the 1978 Boston Symposium, 4% of the papers dealt with radiation effects, while in 1979 and 1980 this number was 9%.

In the United States, the Materials Characterization Center has the responsibility for developing standard tests for irradiation effects. The MCC has chosen to begin by specifying a standard test for the effects of alpha-decay in nuclear waste solids (MCC-6). We agree with the priorities inherent in this choice. Availiable evidence strongly suggests that, as a rule, effects associated with internal alpha-decay have the greatest potential for affecting waste form durability. Moreover, there is a need to establish testing procedures promptly, since times of one year or longer may be required to achieve laboratory doses equivalent to those anticipated in a repository

Having proposed a standard test, the MCC convened a workshop at which the proposed test and other issues relevant to radiation testing were discussed. We will not comment further here on the general discussions except to say that they are both lucid and thorough while raising no issues which were not addressed in our earlier review under the present task. The MCC-6 test is discussed below.

4.4.9.2 MCC-6: Standard Test for the Effects of Alpha Decay in Nuclear Waste Solids

The version of MCC-6 proposed to the participants of the July 1980 workshop was drafted in March 1980.[114] This test uses the actinide doping method (^{244}Cm).

The basic test technique involves periodically performing various measurements on the sample as the density of alpha decays builds up with time. Comparison measurements are carried out on undoped samples. Specific measurements proposed in the March 1980 draft include those shown in Table 4.3.

In a more recent version of MCC-6 drafted in December 1980, only tests (1) and (7) have been retained.[149] The dopant may be either ^{240}Cm or ^{238}Pu; no fixed dose is required - the doping level is to be adjusted so that alpha-decay doses equivalent to the 10^6 year dose in a particular waste form can be achieved in a "reasonable length of time." This represents a departure from the earlier draft (March, 1980), where the objective was to test at doses (6×10^{18} α/cm^3) where saturation in density changes and stored energy buildup are commonly observed.

We feel that the earlier version of MCC-6 (March 1980) was superior to the December 1980 draft from the viewpoint of test development. One virtue of the March 1980 draft is that it incorporates a number of analytical techniques which are potentially useful in mechanistic investigations. There is still a good deal we do not know about the details of damage formation by internal alpha decay. (See section 4.4.10) Moreover, to the best of our knowledge, tests of the sort proposed in MCC-6 have been largely restricted to borosilicate glass at this point; almost no data are available on the leaching of internally doped ceramic waste forms. Consequently, it seems prudent, particularly in view of the complications involved in sample preparation and the time required for testing, to extract as much information as possible from each test. In particular, it may be important at some future time to consider

why leach rate or density changes occur under irradiation, in order to relate laboratory experiments to field conditions, or to weigh the implications of unanticipated results.

Table 4.3

Tests Proposed in MCC-6, March 1980 Version[114]

	Test	Analysis Frequency
1.	Static Leach Test (MCC-1)	Initially; at max. dose
2.	High Flow Rate Lech Test (MCC-2)	Initially; at max. dose.
3.	Compressive Strength Test (MCC-9)	Initially; at max. dose.
4.	X-Ray Diffraction Analysis (MCC-SM-5)	Initially; once per month to max. dose.
5.	Scanning Electron Microscopy (MCC-SM-6)	Initially; once per month to max. dose.
6.	Optical Microscopy (MCC-SM-7)	Initially; once per month to max. dose.
7.	Density Measurement (MCC-SM-8)	Initially; once per month to max. dose.
8.	Stored Energy by Differential Scanning Calorimetry (MCC-SM-9).	Initially; once per month to max. dose.

The initial idea of carrying out measurements at doses in the saturation regime is also appealing. The saturation level is a physical parameter which may be quite useful if further kinetic analysis is required (see section 4.4.10). The reason for relaxing this requirement in favor of the million year dose apparently involves the idea that greater laboratory doses are of no practical interest from the perspective of repository performance. However, it has not been established that a "million year" dose administered in the laboratory time frame ($\sim$1 year) is equivalent, in radiation damage terms, to the same dose administered over one million years in the repository. There is reason to expect that experiments at high dose rates might in fact overestimate the damage produced in the repository [98]. However, as suggested in the MCC workshop proceedings, this must be confirmed[144].(see section 4.4.10.)

Finally, another point may be worth considering. As the MCC emphasizes there is nothing which prevents tests such as those outlined earlier from being carried out in conjunction with those minimally required in the present draft version of MCC-6. For licensing purposes, perhaps a more comprehensive version of MCC-6 could be developed, which requires the demonstration of some predictive capability. The time scale of the MCC-6 test is such that early data can be analyzed and projections made while the test is still ongoing. The demonstrated ability to predict test results would weigh heavily in establishing the validity of performance assessments.

4.4.10 Review and Discussion of Issues in Test Development

In this section we assess the current state of radiation test development. Specifically, we discuss those issues bearing on the development of tests which might produce the quantitative performance data requisite for licensing. A large number of tests have been carried out within the DOE community and other laboratories. Progress over the last year has been encouraging. Generally, in scope and intent, these tests reflect a serious committment toward understanding the effects of radiation on waste forms. At this point, however, we are not able to stipulate which tests, if any, would be acceptable for licensing performance evaluations. There are several promising candidates. In addition, a fairly broad testing experience now exists which allows identification of the general types of tests which may be required. Outstanding issues remain, however, which should be addressed before a particular test can be qualified for licensing applications. These are discussed below.

4.4.10.1 Internal vs. External Irradiation

Both internal doping (as recommended in MCC-6) and external radiation have been used to study effects associated with internal alpha decay in waste forms. Evidently the different techniques may produce dramatically different results. In at least two cases, results obtained by ion-implantation techniques are said to hold serious implications for the durability of waste glasses against internal alpha decay.[108-111] Tests on samples internally doped with alpha emitters commonly fail to show evidence of any serious effect on leachability[30,97,98,103-106,139]. Two questions then arise: first, why are the results different for different testing techniques and, second, which technique best reflects field conditions. We have considered these questions in some detail[150].

Dran, et al. describe measurements in which the effects of radiation damage due to alpha-recoil nuclei in waste forms are simulated by external heavy ion implantation.[108-110] This produces a thin ($\sim$ 500 A) damaged region at the implanted surface. The chemical durability of the damaged region is then investigated by a profiling technique, which compares the etch rates of irradiated and unirradiated regions. They define a "critical" ion fluence of approximately 5×10^{12} ions/cm^2. For fluences below this value, the durability of the glasses is said to be unaffected, in accord with earlier work on samples doped with alpha-emitters. For fluences above this "critical" value, etching rates of all glasses may undergo a drastic increase in etch rate (>20x).

In the absence of a standardized leach test for implanted and internally doped samples, one can only speculate on the extent to which different conclusions reflect different test conditions. It has been implied that the effects observed in implantation experiments have gone undetected in experiments with doped waste glasses because the alpha-decay dose was too low. This is not the case. We calculate that the "critical" implantation dose of 5×10^{12} ions/cm^2 corresponds to an implantation density of approximately 10^{18}/cm^3. Measurements in the U.K.,[30] in Germany,[103] and in the U.S.[104,139] have been carried out on waste glasses which have undergone substantially more than 10^{18} internal alpha decays/cm^3. These do not indicate a drastic increase in leach rate.

The most recent implantation data indicate a strong dependence on both leaching conditions and on sample type. Certain glasses show a strongly enhanced etching in NaCl brine at 100°C following a "critical" implantation dose, while others do not. Similarly, the results in DIW at 100°C may show only a modest leachability increase, (approximately three times) in contrast to that seen with brine (approximately 50 times). It is possible that some of the differences between results obtained with implanted and with doped glasses stem from differences in the measurement technique. If we assume that the effect of irradiation actually enhances the initial removal rate of a thin surface layer, this might very well go overlooked in conventional measurements. The etching technique used in implantation studies is exceptionally sensitive to such effects. However, it is questionable as to whether the heavy ion implantation technique does in fact properly simulate the radiation damage anticipated due to alpha recoils in HLW glasses. For example:

- The implantation technique produces only a thin surface damage layer. Irradiation induced dimensional changes occur in the irradiated glass. Such changes in a thin surface layer may produce local stresses which affect chemical durability. These stresses would be absent in homogeneously irradiated material.

- The high dose rates employed in implantation techniques may swamp slow (thermal) annealing processes operable over months or years. Annealing processes have been postulated to explain saturation effects commonly observed in internal alpha decay damage, but only limited data are available. It has been suggested that alpha particles might anneal alpha-recoil damage. Such annealing would, of course, be absent in ion-implantation experiments described here.

- Ion implantation does not reflect the stochastic nature of internal alpha decay. For a given implantation density,the number of heavy particles which penetrate the surface will be about 8 times greater than for a sample which has undergone an equivalent density of alpha-decays.

- Ion implantation may produce local heating and charging effects. The relative significance of these effects is difficult to estimate <u>a priori</u>.

- Quite commonly, initial leach rates are substantially greater than the steady-state or asymptotic values which should be used for long-term projec-

tions. Moreover, establishment of asymptotic conditions may require weeks or months, and the buildup of leach layers thousands of angstroms thick.(Section 4.2) It is difficult to see how the implantation technique, in which the damage is restricted to a layer 500 A thick, could in general provide an accurate basis for long-term extrapolation.

Hirsch [111], describes a corrosion process for glass which involves surface sensitization by (vacuum) bombardment with ions, electrons or photons. This sensitization is said to take place preferentially at microstructural discontinuities. Subsequently, alkali ions migrate to the sensitized sites and are reduced. The reduced alkali metal reacts with water vapor and is removed from the glass. A cyclic hydrolysis reaction is then initiated at the uncompensated alkali ion sites resulting in enhanced corrosion. The surface sensitization is said to require a minimum (or threshold) irradiation dose. In the experiments described, this threshold dose is estimated as 10^{16} ions/cm^3.

Again (in contrast to the claims in reference 111) the proposed mechanism has not been corroborated in tests on internally doped samples. Irradiation induced alkali atom migration has been returned to earlier.[126] A major difficulty in comparing the two techniques is that one has almost no guidance on the dosimetric equivalance between the 2 keV Ar ions used in Hersch's experiment and the alpha particles and recoil nuclei produced in internal alpha decay. For example, an ion fluence of 10^{16} ions/cm^2 would be produced by about 2-3 x 10^{18} α/cm^3. An equivalent number of atomic displacements would be produced by about 10^{20} α/cm^3. This latter dose is far beyond that which is anticipated in HLW forms after 10^6 years. Further, the reported surface sensitization apparently takes place during vacuum irradiation at high dose rates. Irradiation in repository atmospheres and repository dose rates might significantly affect surface sensitization, by virtue of charge transfer and annealing. Consequently, the relevance of the Ar-ion implantation experiment to repository conditions is difficult to establish.

We have set down these comments in more detail elsewhere[150]. Our views, arrived at independentely, coincide to a considerable degree with those of other reviewers in the DOE and abroad[151,152]. We feel, then, that internal alpha doping should presently remain the preferred method for quantitative performance assessment. Internal fission and neutron irradiation are not recommended for critical evaluations of alpha decay damage (see section 4.4.10.7).

To maintain perspective on the difference between external ion bombardment and internal alpha decay, it should be pointed out that in leach testing only a thin surface layer is commonly examined. In external implantation experiments, it is certain that at least some of this surface has been directly irradiated. In experiments with internal alpha emitters, however, the range of the alpha recoil is extremely short (approximately 250 A). Consequently, even a very local (approximately 1000 A) depletion of radionuclides could result in a reduced radiation dose in the region being leached. It is not clear from the literature that this point has received the attention it deserves; many authors do not report a specific radionuclide depth profile in

their doped samples. Since test glasses may be doped with alpha emitters to near their solubility limits, a potential source of systematic error exists. Therefore, steps must be taken to ensure that the spatial distribution of radionuclides and displacement damage in or near the region under test does indeed reflect the situation anticipated in actual waste forms. Leach testing should be carried out on material which is characteristic of bulk and surface regions of the manufactured waste form. Very-near surface regions may not be entirely characteristic of bulk behavior since recoil nuclei can be ejected from surfaces during alpha decay.[153] There is also evidence that selective chemical attack occurs along recoil nucleus and heavy ion tracks at surfaces.[154,155] As a minimum requirement, the material should be leached to a depth of several recoil "tracks".

4.4.10.2 Radiation Dose Rate Effects

The relative importance of radiation dose rate effects is a major unresolved issue in radiation test development. We believe that at some point all waste package materials should be exposed to total radiation doses typical of those anticipated in the repository configuration. This will be necessarily involve administering the radiation dose at dose rates which are at least hundreds, if not thousands, of times greater than those encountered in the repository. We recommend that research be conducted to determine, as comprehensively as possible, whether the production of radiation damage at high dose rates does in fact represent worst case conditions.

The most straightforward way to do this is to compare the radiation damage formed at the same total dose for different dose rates. In practice, however, it is often difficult or impossible to vary the dose rate over a sufficiently wide range, without resorting to different types of irradiation. This is probably the case for internal alpha decay. Under these conditions, one should attempt to establish the dose rate scaling from a mechanistic viewpoint. For example, if the apparent saturation of stored energy buildup or swelling in waste forms is simply due to statistical limitations on the number of available sites for displaced atoms, dose rate effects may be negligible. On the other hand, if over long periods of time processes can occur whereby the number of sites for displaced atoms is increased (through formation of aggregates by diffusion of point defects, for example), experiments at high dose rates may underestimate the radiation damage formed in the repository; this could be counterbalanced by slow thermal annealing. Research should address these mechanistic considerations, specifically considering the need to establish worst case conditions for testing. Studies of temperature effects may be particulary helpful here.

4.4.10.3 Temperature Effects

Very little is known about the temperature dependence of radiation damage formation in actual waste form materials. It is sometimes assumed that radiation damage levels will decrease monotonically as the temperature increases.

This may be true in some cases; in others, radiation damage formation may increase with increasing temperature over a certain region[121].

Temperature effects may also be important from a mechanistic viewpoint. The majority of internal alpha decays will occur under ostensibly isothermal conditions. Consequently, testing over an extensive temperature range might appear unnecessary for alpha decay effects. However, tests at different temperatures might provide important mechanistic information to aid in relating laboratory results to repository conditions. For example, Weber, et al. found that alpha-decay-induced swelling in a number of materials could be empirically described by simple saturating exponential expressions, and phenomonologically interpreted the parameters.[133] The saturation must result from a balance of defect formation and recombination (annealing) processes. It would be extremely useful to learn if the recombination processes represent ordinary thermal annealing, or whether they are athermal and induced by the radiation itself. In the latter case, if the annealing rate depends nonlinearly on radiation dose rate, one might anticipate increased radiation damage under repository conditions. This question could be studied by observing the temperature dependence of saturation levels and/or pulsed annealing following irradiation.

The results of measurements such as those described above might usefully be correlated with stored energy release as determined by thermal analysis. In addition, we believe that thermal measurements will be extremely useful in studying possible irradiation induced phase changes. For example, the metamict state produced in certain minerals by irradiation over geologic time could differ from that produced by irradiation on the laboratory time scale, since the metamict state is not structurally unique. If it could be established that the two are in fact equivalent, it would strengthen our confidence in extrapolating laboratory results to geologic times. The equivalence could be examined by determining if the same correlation exists between density changes and stored energy release in laboratory and natural samples. We also feel that confirmatory DTA measurements would be instrumental in establishing whether waste glasses exhibit any tendency toward radiation-induced devitrification. Devitrification kinetics can be compared in irradiated and unirradiated glasses. Some work in this area has recently been reported.[151]

4.4.10.4 Ionization in the Waste Form

We have indicated earlier (section 4.4.5) that the possible structural effects of ionizing radiation require detailed consideration; further a leach test should assure that the charge states of radionuclides and other species in the waste form do in fact simulate those which are anticipated in the presence of radiation in the repository.

In addition, leach tests to study the effects of alpha recoil damage are often carried out in waste forms which have not been subjected to gamma radiation. Under actual repository conditions, the waste form will have received a substantial gamma dose before alpha recoils build up to the values commonly used in tests (Figures 4.4 and 4.5). The possible effects of gamma-ray

"preconditioning" should be established in tests designed to study long term leaching. There is some evidence to indicate that ionization may tend to offset certain effects such as swelling, which are produced by displacement damage.[158,159] We are not aware of any direct studies on waste form materials. It has been suggested that ionization might play a role in radiation annealing. Of course, the ionization from fission fragment decay will persist for a relatively short time with respect to that required for the build-up of alpha decays.

4.4.10.5 Radiation Induced Stresses

There is a growing body of evidence which indicates that bulk or differential radiation-induced volume changes may be anticipated in many waste forms. We feel that this may be one of the more potentially significant effects associated with irradiation, particularly in multiphase systems such as SYNROC, or barrier materials such as high silica-coated porous glass; differential stresses could result in microfracture or cracking within the waste form, or in unacceptable stress levels in barrier materials. At present, however, there is almost no information by which to relate the swelling or compaction observed in laboratory samples to the amount of structural damage to be expected in actual waste forms. This damage may depend sensitively on material composition, grain size, radionuclide distribution and waste form geometry.

We feel that a bounding analysis might be useful in defining those cases where further critical evaluation is needed. For example, one could calculate the radiation-induced stresses for a particular configuration using highly conservative assumptions as to the extent of the anticipated volume changes and material strengths. In some instances, such screening calculations may be adequate to dismiss the possibility of extensive radiation-induced waste form or barrier fracture.[137]

Our own first order, highly simplified analysis of the possible consequences of radiation induced stresses in waste package components,[163] indicates that more detailed consideration is indeed warranted in certain areas. Radiation induced stresses are being explicitly considered in an NRC sponsored research program at Iowa State University.[138]. The radiation induced volume changes are taken to vary with temperature (by virtue of relaxation processes) leading to differential stresses. The present model would apply primarily to beta-gamma damage. Significant volume changes may also occur under isothermal conditions due to alpha-decay damage after about the first 1000 years. In this region, it would probably be necessary to extend the model.

It is encouraging to learn that the effect of gamma radiation on the density of borosilicate waste glass is presently being studied at SRL.[131] To maintain perspective, we reiterate that the one experiment where differential radiation-induced swelling was intentionally introduced did not indicate that the resulting microfracture affected leach rates.[104]

4.4.10.6 Simulating Transmutations

At this point, the data on transmutation effects are extremely limited. Only one direct investigation has been carried out, and the experimental technique has some uncertainties. For example, the reactor irradiation introduces damage, requiring that the samples be annealed at high temperature before the beta transmutation buildup. Also, most of the beta transmutations in the waste form will occur at elevated temperature, which may be somewhat different than the storage temperatures in the present experiments. It is hard to say what effect, if any, these factors may have on the relevance of test results. It would seem that some sort of thermal analysis could be undertaken to determine, for example, if precipitates or different phases might be induced by transmutation at higher temperatures.

It may be worthwhile to consider other methods of simulating transmutations. One could prepare waste forms containing various concentrations of transmutation products and observe the resultant structural alteration. One example is the study performed by R. S. Roth, et al. of NBS in the systems K-Al-Si-O and Ca-Al-Si-O. These systems readily simulate radwaste fixation conditions with the substitution of K for Cs and Ca for Ba. Both radius change and valence change are identical to those for the Cs-Ba transmutation.

For such simulation by crystal chemistry to be valid, the transmuted element should be mobile enough to sample a number of sites in the actual waste form, as would occur during the preparation of simulated waste forms containing transmutation products. Our preliminary estimates imply that the desired fast solute mobility may exist in the waste form, rationalizing the simulation of transmutations by crystal chemistry. A more comprehensive conclusion may be arrived at after collecting further diffusion data in more complicated mineral systems.

4.4.10.7 Fission Fragment Effects

Recently, Vance and Pillay have considered simulating internal alpha decay by (externally induced) internal fission in ceramics.[130] They conclude that fission fragment irradiation is probably not a good simulation of alpha-recoil damage. The difficulty is that sensitivity to fission fragment irradiation does not necessarily imply sensitivity to alpha-recoil irradiation. More interestingly, however, they cite evidence to suggest that in certain cases the relative importance of fission fragments may be underestimated in calculations such as those leading to Figure 4.4. In natural zircon, for example, they argue that, in relation to alpha decay, spontaneous fission may produce (net) damage with an efficiency which is up to 1000 times greater than anticipated.

There are several reasons why this could occur. Damage production by fission fragments and alpha recoils is ordinarily quite different. The former frequently leads to formation of etchable "tracks" while the latter, at least, for the most part, may not. (However, see Section 4.4.10.1 and Reference 160). Fission fragments tracks result, it is believed, from ionization effects not

accounted for in "knock on" calculations. The dimensions of fission fragment and alpha-recoil tracks would be very different[161]. Consequently, it may be that due to differences in annealing or other effects, displaced atoms produced by fission fragments are not equivalent to those generated in internal alpha decay for net damage formation. In fact, this equivalence may vary from material to material, and depend on the type of damage which is being observed.

The evidence which Vance and Pillay present to suggest an enhanced role for spontaneous fission in HLW forms is sketchy. The implications for waste form durability are by no means clear. Certainly we would expect the relative importance of spontaneous fission and beta-gamma decay to be increased in systems which are susceptible to ionization damage. Even a thousandfold increase, however, would still leave alpha-decay as the dominant source of atomic displacements. The implications for test development, however, are clear enough. Figures such as Figure 4.4 may be misleading unless:

1. Both knock-on and ionization induced atomic displacements are accounted for.

2. It is recognized that the fate of the displaced atoms may depend on the manner in which they are produced.

3. One considers the relationship between the possible configurations of displaced atoms and the engineering properties of interest.

Finally, it is worthwhile to point out that in a recent study on UO_2, Weber found that fission fragment damage was less efficient than anticipated on the basis of internal alpha-decay.[133] Evidently, generalizations are risky.

4.4.11 Conclusions and Recommendations

In this section, we summarize our views on recommended tests and/or research needed to develop the requisite tests.

4.4.11.1 Radiation/Leach Testing

Tests will be required to evaluate the effect of internal alpha decay, ionizing radiation and internal transmutations on leach rates. A number of scoping and comparative tests exist. The effects of leachant radiolysis should also be evaluated in assessing leach resistance.

Tests under development, such as MCC-6, have the potential for developing the requisite information for licensing. However, research should be carried out to qualify these tests. In particular:

(1) The effect of radiation dose rates on radiation damage formation and solution radiolysis should be evaluated.

(2) The effects of temperature on radiation damage formation should be evaluated.

(3) Leach tests should specifically evaluate the possible consequences of radiation induced stresses and microfracture in inhomogeneous or multibarrier waste forms.

• Internal doping is the recommended method for simulating internal alpha decay or spontaneous fission. However, while the quantitative correspondence between internal alpha decay and heavy ion implantation is questionable, the French workers have raised an important issue which warrants further attention. Essentially, they have asked whether or not highly etchable damage tracks can be formed by alpha-recoil nuclei in waste glasses. We do not know of any direct observations of alpha-recoil tracks in glasses. However, such etchable tracks have been reported in minerals and their implications for radioactive waste storage discussed.[160] Due to the complex nature of track formation, it may in fact be that etchable tracks are formed in waste forms under some conditions.[161] (Section 4.4.10.1.)

• We feel that it is essential that the difference between results obtained with ion-implanted and with internally doped samples be thoroughly understood. This will require a detailed characterization and comparison of the radiation damage produced by each technique, under standard test conditions. We understand that work along these lines is currently underway in DOE Laboratories[131]. We also recommend that such a comparison also be carried out for samples damaged by neutron irradiation or internal fission (a good start here has been made in Europe). This work may lead to the establishment of a reliable screening procedure, which could preceed or even preclude tedious testing with doped waste forms. (Section 4.4.10.1.)

What we consider here is not a trivial undertaking. It is not yet obvious how best to characterize the radiation damage formed by the different techniques. Both bulk and surface sensitive measurements will probably be required. We envision the various samples subjected to a common test of chemical durability, which may differ in some respects for standard leach tests. Alpha particle effects and helium buildup may be studied by alpha bombardment either prior or subsequent to neutron or heavy particle bombardment.

• Leach tests probe only a thin surface region; consequently, the radionuclide distribution in the region under study should be carefully characterized. Both bulk and surface regions of large samples should be investigated. In particular, in samples where radionuclides may be retained in altered structures produced by incongruent dissolution, the radiation durability of these structures should be examined.

4.4.11.2 Radiation/Physical Property Testing

• From the repository design viewpoint, the most important structural effect of radiation may involve density changes (and attendant generation of internal stresses). The effect of both ionizing radiation and internal alpha

delay on density should be determined for candidate waste form materials. Again, scoping and comparative tests are available, but research on dose rate effects, relaxation, etc. will be necessary to relate these results to repository conditions. (Section 4.4.10.2, 4.4.10.4.)

- Testing will be required to evaluate the possiblity and consequences of radiation induced microfracture in radionuclide host phases or inert barriers. This will require a knowledge of radiation-induced expansion coefficients and the details of the anticipated radionuclide distribution. Uniform irradiation (e.g. neutron bombardment) will not provide an acceptable simulation for critically evaluating microfracture in inhomogeneous waste forms. (Section 4.4.10.5.)

- Mechanical tests should be carried out to determine if the mechanical durability of radionuclide host phases will be seriously affected by irradiation. Such tests should consider separately the cases where helium is either retained in or released from the waste form. Test development is required on this area.

4.4.11.3 Other Testing Recommendations

- Special efforts should be devoted toward identifying those cases where the waste form may be susceptible to ionization damage. These efforts should include: (1) determining the effect of ionizing radiation alone at repository doses (10^{12} rad) and (2) determining if the formation of alpha decay damage will be affected by a prior dose of beta-gamma irradiation. It should also be recognized that alpha particles and fission fragments deposit most of their energy, non-uniformly by ionization processes. Bulk comparisons on a per-rad basis may not reflect the highly local nature of energy deposition, which can lead to tracks in some materials. (Section 4.4.10.4, 4.4.10.7.)

- The development of techniques to investigate transmutation effects is still at an early stage. Additional emphasis should be placed here, including temperature studies and the possibility of simulation by chemical methods. (Section 4.4.10.6.)

- Thermal studies should receive increased emphasis in test development, both to span anticipated repository conditions, and to aid in developing mechanistic insight. Thermal studies may be particularly useful in evaluating susceptibility to radiation-induced phase changes. (Section 4.4.10.3.)

- The relative importance of spontaneous fission should be reconsidered and, where such consideration proves inconclusive, examined by direct experiment. Doping isotopes such as ^{244}Cm can undergo spontaneous fission as well as alpha decay. (Section 4.4.10.7.)

4.5 References

1. R. H. Doremus, "Chemical Durability in Glass," in Treatise on Materials Science and Technology, Vol. 17, M. Tornozawa and R. H. Doremus, Eds., (Academic Press, New York, 1979) p. 41.

2. R. H. Doremus, Glass Science, Wiley, N. Y., 1973.

3. D. E. Clark, M. F. Dilmore, E. C. Ethridge and L. L. Hench, "Aqueous Corrosion of Soda-Silica and Soda-Lime-Silica Glass," J. Amer. Ceram. Soc. 59, 62 (1976).

4. L. L. Hench and D. E. Clark, "Physical Chemistry of Glass Surfaces," J. Non-Crystalline Solids 28, 83-105 (1978).

5. R. W. Douglas and T. M. El-Shamy, "Reactions of Glasses with Aqueous Solutions," J. Amer Ceram. Soc. 50, 1 (1967).

6. D. E. Clark and E. Lue Yen-Bower, "Corrosion of Glass Surfaces," Surface Science 100, 53 (1980).

7. D. E. Clark, E. Lue Yen-Bower and L. L. Hench, "Corrosion Behavior of Zinc Borosilicate Simulated Nuclear Waste Glass," in Ceramics in Nuclear Waste Management, DOE Conference Proceedings CONF-790429, May 1979, p. 256.

8. B. T. Kenna and K. D. Murphy, "Long Term Soxhlet Tests," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

9. L. R. Pederson, M. T. Thomas and G. L. McVay, "Application of ESCA to Corrosion Studies of Glasses Containing Simulated Nuclear Wastes," J. Vac. Sci. Technol. 18, 732 (1981).

10. H. W. Nesbitt, G. M. Bancroft, W. S. Fyfe, S. N. Karkhanis, A. Nishijima and S. Shin, "Thermodynamic Stability and Kinetics of Perovskite Dissolution," Nature 289, 358 (1981).

11. D. G. Coles and F. Bazan, "Continuous-Flow Leaching Studies of Crushed and Cored SYNROC," Lawrence Livermore Laboratory Report UCRL-84679, 1980.

12. Office of Nuclear Waste Management, Technical Progress Report for the Quarter July 1 - September 30, 1979, Report ONWI-9(4), p. 163 (1979).

13. W. Stumm and J. J. Morgan, Aquatic Chemistry - An Introduction Emphasizing Chemical Equilibria in Natural Waters, 2nd Ed., Wiley-Interscience, New York, 1981.

14. R. Wang and Y. B. Katayama, "Electrochemical Methods for In-Situ Leaching of Spent Fuel," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

15. J. A. Stone, "Factors Affecting the Leachability of Nuclear Waste Forms," Abstract, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

16. D. D. Walker, J. R. Wiley, M. D. Dukes and J. R. LeRoy, "Leach Rate Studies on Glass Containing Actual Radioactive Waste," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

17. B. T. Kenna and K. D. Murphy, "Mechanism for Elevated Temperature Leaching," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Ed., (Plenum Press, New York, 1980), pp. 191-98.

18. F. B. Walton and W. F. Merritt, "Long Term Extrapolation of Laboratory Glass Leaching Data for the Prediction of Fission Product Release Under Actual Groundwater Conditions," in Scientific Basis for Nuclear Waste Management, V. 2, C. J. M. Northrup, Ed., (Plenum Press, New York, 1980), pp. 155-66.

19. J. D. Tewhey, C. L. Hoenig, H. W. Newkirk, R. B. Rozsa, D. G. Coles and F. J. Ryerson, "The Application of SYNROC to High Level Defense Wastes," in Alternate Nuclear Waste Forms and Interactions in Geologic Media, DOE Conference Proceedings CONF-8005107, April 1981, p. 4.

20. "Composite Quarterly Technical Report Long-Term High-Level Technology, January - March 1980," E. I. du Pont de Nemours & Co., Savannah River Laboratory Report DP-80-157-1, 1980.

21. J. E. Mendel, "A Review of Leaching Test Methods and the Leachability of Various Solid Media Containing Radioactive Wastes," Pacific Northwest Laboratory Report PNWL-1765, 1973.

22. W. A. Ross, D. J. Bradley, L. R. Bunnell, W. J. Gray, Y. B. Katayama, G. B. Millinger, J. E. Mendel, F. P. Roberts, R. P. Turcotte, J. W. Wald, W. E. Weber and J. H. Westsik, "Annual Report on the Characterization of High Level Waste Glasses," Pacific Northwest Laboratory Report PNL-2625, 1978.

23. L. Kahl, "The Chemical Durability of the HLLW-Borosilicate glasses GP 98/12 and GP 98/26," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

24. H. C. Weed, D. G. Coles, D. J. Bradley, R. W. Mensing and J. S. Schweiger, "Leaching Characteristics of Actinides from Simulated Reactor Waste Glass," in Scientific Basis for Nuclear Waste Management, Vol. 1, G. J. McCarthy, Ed., (Plenum Press, New York, 1979), pp. 141-147.

25. H. C. Weed, D. G. Coles, D. J. Bradley, R. W. Mensing, J. S. Schweiger and J. H. Rego, "Leaching Characteristics of Actinides from Simulated Reactor Waste, Part 2," in Scientific Basis for Nuclear Waste Management, Vol. 2, p.167. C. J. M. Northrup, Jr., Ed., (Plenum Press, New York, 1980).

26. W. B. White, "Dissolution of Crystalline Waste Forms. II. The Role of Temperature in the Dissolution Process," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

27. J. M. Rusin, J. W. Shade, R. W. Kidd and M. F. Browning, "Chemically Vapor Deposited Coatings for Multibarrier Containment of Nuclear Wastes," in Alternate Nuclear Waste Forms and Interactions in Geologic Media, DOE Conference Proceedings CONF-8005107, April 1981, p. 248.

28. A. Paul, "Chemical Durability of Glasses; A Thermodynamic Approach," J. of Materials Science 12, 2246 (1977).

29. F. Lanza and E. Parhisan, "Influence of the Film Formation and Composition on the Leaching of Borosilicate Glasses," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

30. K. A. Boult, J. T. Dalton, A. R. Hall, A. Hough and J. A. C. Marples, "The Leaching of Radioactive Waste Storage Glasses," in Ceramics in Nuclear Waste Management, DOE Conference Proceedings CONF-790429, May 1979, p. 248.

31. J. E. Mendel, W. A. Ross, R. P. Turcotte and J. L. McElroy, "Physical Properties of Glass for Immobilization of High Level Radioactive Waste," Nuclear and Chemical Waste Management 1, 17 (1980).

32. K. D. Reeve, D. M. Levins, E. J. Ramon, J. L. Woolfrey, W. J. Buykx, R. K. Ryan and J. F. Chapman, "The Development and Testing of SYNROC for High Level Radioactive Waste Fixation," Abstracts, ANS Conference on Waste Management '81, Tucson, Arizona, 1981.

33. "Technology for Commercial Radioactive Waste Management," U. S. Department of Energy DOE/ET-0028 (1979).

34. D. G. Coles, H. C. Weed, D. D. Jackson and J. S. Schweiger, "Single-Pass Leaching of Nuclear Melt Glass by Groundwater," in Radioactive Waste in Geologic Storage, S. Fried, Ed. (A.C.S. Symposium Series, Vol. 100, Amer. Chem. Soc., Washington, D. C. (1979), pp. 93-114.

35. P. B. Macedo, Aa. Barkatt, Al. Barkatt, H. Simmons, P. E. Pehrsson and B. Townsend, "A Flow Model for the Kinetics of Dissolution of Nuclear Waste Glasses," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

36. J. R. Wiley and J. H. LeRoy, "Long Term Leach Rates of Glasses Containing Waste," in Ceramics in Nuclear Waste Management, DOE Conference Proceedings CONF-790429, May 1979, p. 284.

37. G. J. McCarthy, S. Komarneni, B. E. Scheetz and W. B. White, "Hydrothermal Reactivity of Simulated Nuclear Waste Forms and Water-Catalyzed Waste-Rock Interactions," in Scientific Basis for Nuclear Waste Management, Vol. 1, G. J. McCarthy, Ed. (Plenum Press, New York, 1979). p. 329.

38. J. H. Westsik and R. P. Turcotte, "Hydrothermal Reactions of Nuclear Waste Solids--A Preliminary Study," Pacific Northwest Laboratory Report PNL-2759, 1978.

39. D. J. Bradley, "Leaching of Fully Radioactive High Level Waste Glass and Waste-Geologic Environment Interaction Studies," in Radioactive Waste in Geologic Storage, S. Fried, Ed., (A.C.S. Symposium Series, Vol. 100, Amer. Chem. Soc., Washington, D.C., 1979), pp. 75-91.

40. K. F. Flynn, L. J. Jardine and M. J. Steindler, "Method for Determining Leach Rates of Simulated Radioactive Waste in Waste Forms," in Radioactive Waste in Geologic Storage, S. Fried, Ed., (A.C.S. Symposium Series, Vol. 100, Amer. Chem. Soc., Washington, D.C., 1979), pp. 115-128.

41. D. E. Clark and L. L. Hench, "An Overview of the Physical Characterization of Leached Surfaces," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

42. A. Barkatt, A. Barkatt, P. B. Macedo, P. E. Pehrson, M. Saleh, C. F. Simmons, J. H. Simmons and H. G. Sutter, "A Constant-Medium International Standards Organization Test for the Evaluation of the Chemical Durability of Nuclear Waste Glasses," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

43. G. L. McVay, W. J. Weber and L. R. Pederson, "Effects of Radiation on the Leaching Behavior of Nuclear Waste Forms," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

44. S. Brunauer, P. H. Emmet and E. Teller, "Adsorption of Gases in Multimolecular Layers," J. Amer. Chem. Soc. 60, 309-19 (1938).

45. B. Lee, "Brighter Future for Nuclear Wastes?," New Scientist, April 23, 1981.

46. R. L. Pecsok, L. D. Shields, T. Cairns and I. G. McWilliam, Modern Methods of Chemical Analysis, Wiley, New York, 1976.

47. W. J. Haas, R. K. Winge, R. N. Kniseley and V. A. Fassel, "Specifications for an Inductively Coupled Plasma Simultaneous Multielement Analysis System," Iowa State University, Ames Laboratory Report IS-4353, 1978.

48. "Composite Quarterly Technical Report, Long-Term High Level Waste Technology, October-December 1980," Savannah River Laboratory Report DP-80-157-4, 1981.

49. S. Elchuck and R. M. Cassidy, "Separation of Lanthanides on High-Efficiency Bonded Phases and Conventional Ion Exchange Resins," Anal. Chem. 51, 1434 (1979).

50. R. M. Cassidy and S. Elchuck, "Trace Enrichment Methods for the Determination of Metal Ions by High Performance Liquid Chromatography," J. Chromatographic Sci. 18, 217 (1980).

51. W. Christie and J. E. Carter, "Resin Bead Technique for Mass Spectrometric Analysis of Actinides," Anal. Letters 14, 239 (1977).

52. D. E. Clark, C. G. Pentano and L. L. Hench, Corrosion of Glass, Books for Industry and the Glass Industry, New York, 1979.

53. N. S. McIntyre, G. G. Strathdee and B. F. Phillips, "Secondary-Ion Mass-Spectrometric Studies of the Aqueous Leaching of a Borosilicate Waste Glass," Surface Science 100, 71 (1980).

54. B. W. Veal, D. J. Lam, A. P. Paulikas and D. P. Karim, "X-Ray Photoelectron Spectroscopic Studies of Silicate Glasses: Implications to Bonding and Leaching," Nucl. Technol. 51, 136 (1980).

55. D. J. Lam, B. W. Veal, H. Chen and G. S. Knapp, "Bonding of Metal Oxides in Sodium Silicate Glass," in Scientific Basis for Nuclear Waste Management, Vol. 1, G. J. McCarthy, Ed., (Plenum Press, New York, 1979).

56. Materials Characterization Center, "MCC-1 Static Leach Test," August 1980. (Draft submitted to the Materials Review Board.)

57. International Atomic Energy Agency, "Leach Testing of Immobilized Radioactive Waste Solids, A Proposal for a Standard Method," E.D. Hespe, Ed., Atomic Energy Review 9, 195-207 (1971).

58. International Standards Organization, 5/N 38, "Long-Term Leach Testing of Radioactive Waste Solidification Products," ISO/TC 85/SC 5/WG 5/N 38, Berlin, West Germany.

59. ANSI/ASTM C-225-73, 1978, "Standard Test Methods for Resistance of Glass Containers to Chemical Attack," American Society for Testing and Materials, Philadelphia, Pennsylvania.

60. O. U. Anders, et al., "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes," (first draft of a standard), ANS Working Group ANS-16.1, American Nuclear Society, 1979.

61. J. K. Johnstone, "Interim TRU Waste Leach Test," Sandia Laboratories, Albuquerque, New Mexico, 1979.

62. S. R. Scholes, Modern Glass Practice, Industrial Publications, Chicago, Illinois, 1951, pp. 264-265.

63. International Standards Organization, 5/N 40, "Soxhlet Leach Test Procedure for Testing of Solidified Radioactive Waste Products," ISO/TC 85/SC 5/WG 5/N 40, Berlin, West Germany.

64. J. H. Westsik, "Leaching Studies," in Annual Report on the Development and Characterization of Solidified Waste Forms for High-Level Wastes, Pacific Northwest Laboratory Report PNL-3060, 1978.

65. D. J. Bradley, G. L. McVay and D. G. Coles, "Leach Test Methodology for the Waste/Rock Interactions Technology Program," Pacific Northwest Laboratory Report PNL-3326, 1980.

66. L. C. Watson, A. M. Aiken and A. R. Bancroft, "The Permanent Disposal of Highly Radioactive Wastes by Incorporation Into Glass," Atomic Energy of Canada Ltd. Report AECL 1072, 1960.

67. A. R. Bancroft, "The Incorporation of Fission Products into Glass for Disposal," Can. J. Chem. Eng., 19 (February, 1960).

68. K. B. Harvey, "An Intercomparison of Leach-Testing Methods, and the Effects of Waste Form Composition on Test Duration," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

69. D. J. Bradley, C. O. Harvey and R. P. Turcotte, "Leaching of Actinides and Technetium from Simulated High-Level Waste Glass," Pacific Northwest Laboratory Report PNL-3152, 1979.

70. H. C. Weed and D. D. Jackson, "Design of a Variable Flow-Rate, Single-Pass Leaching System," Lawrence Livermore Laboratory Report UCRL-52785, 1979.

71. F. Lanza and E. Parnisari, "Evaluation of Long-Term Leaching of Borosilicate Glass in Pure Water," in Ceramics in Nuclear Waste Management, U. S. DOE Conference Proceedings CONF-790420, May 1979, p. 238.

72. B. E. Paige, "Leachability of Glass Prepared From Highly Radioactive Calcined Alumina Waste," Phillips Petroleum Co., Atomic Energy Division Report IDO-14672, 1966.

73. J. A. Kelly and R. M. Wallace, "Procedure for Determining Leachabilities of Radioactive Waste Forms," Nuclear Technology 30, 47-51, 1976.

74. D. M. Strachen, B. O. Barnes and R. P. Turcotte, "Standard Leach Tests for Nuclear Waste Materials," Abstracts, Scientific Basis for Nuclear Waste Management, Materials Research Society Annual Meeting, Boston, November 1980.

75. J. E. Mendel, Ed., "Materials Characterization Center Workshop on Leaching of Radioactive Waste Forms, Summary Report," Pacific Northwest Laboratory Report PNL-3318, April 1980.

76. N. S. McIntyre, S. Sunder, D. W. Shoesmith and F. W. Stanchell, J. Vac. Sci. Technol. 18, 714, 1981.

77. Materials Characterization Center, "MCC-1 Static Leach Test," January 1981. (Draft Submitted to the Materials Review Board.)

78. A. J. Machiels, "Short-Term Leaching Behavior of Waste Forms - A Potential Area for Improvement," in Alternate Nuclear Waste Forms and Interactions in Geologic Media, ORNL and DOE Conference Proceedings CONF-8005107, May 1980, p. 70.

79. H. C. Claassen, "Conceptual Models Governing Leaching Behavior and Their Long-Term Prediction Capability," Abstracts, ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 1980.

80. T.-M. Ahn, Brokhaven National Laboratory, memo to file, June 1, 1981.

81. ASTM C773, "Standard Test Method for Compressive (Crushing) Strength of Fired Whiteware Materials", 1979.

82. ASTM C158, "Standard Methods of Flexure Testing of Glass", 1972.

83. Materials Characterization Center, MCC-11, "Tensile Strength Test," Pacific Northwest Laboratory Draft Report, December 1980.

84. R. H. Marion and J. K. Johnstone, "A Parametric Study of the Diametral Compression Test for Ceramics," Sandia Laboratory Report SAND-75-0347, 1975.

85. ASTM E680-79, "Standard Test Method for Drop Weight Impact Resistivity of Solid-Phase Hazardous Materials".

86. ASTM C368-77, "Standard Test Method for Impact Resistance of Ceramic Tableware".

87. L. J. Jardine and W. J. Mecham, "Impact Tests and Impact Analysis Methodology for Solid Waste Form", presented at ANL MCC Workshop on the Mechanical Property of Nuclear Waste, March 1981.

88. W. J. Mecham, L. J. Jardine, R. H. Pelto and M. J. Steindler, "Characterization of Impact Fracture of Brittle Solid Waste Forms," presented at the Materials Research Society Meeting, Boston November 1979.

89. W. J. Mecham, L. J. Jardine and M. J. Steindler, "The Effect of Impact Energy on Solid Waste Composits of Brittle and Ductile Materials," in Ceramics in Nuclear Waste Management, U. S. D.O.E. Conference Proceedings CONF-790420, May 1979, p. 327.

90. G. Bandypadhyay, Argonne National Laboratory, Intra-laboratory Memo, 1981.

91. D. G. Atteridge and G. B. Dudder, "MCC-10, Brittle Materials Impact Test," Pacific Northwest Laboratories.

92. "Composite Quarterly Technical Report, Long-Term HLW Technology," April-June, Savannah River Report DP-80-157-2, 1980.

93. S. C. Slate, L. R. Bunnel, W. A. Ross, F. A. Simonen and J. H. Westsik, Sr., "Stress and Cracking in HLW Glass," Pacific Northwest Laboratories Report, PNL-SA-7369, 1978.

94. Materials Characterization Centre, Proceedings of the MCC Workshop on the Mechanical Properties of Nuclear Waste, March 1981.

95. S. W. Freiman, "Fracture Mechanics of Glass," in Glass: Science and Technology, ed. by D. R. Uhlmann and N. J. Kreidl, eds. (Acedemic Press, New York, 1980 pp. .

96. H. Tada, P. C. Paris and G. R. Irwin, "The Stress Analysis of Cracks Handbook," Del Research Corporation, Hellertown, Pa., 1973.

97. J. E. Mendel, et al., Pacific Northwest Laboratory, "Annual Report on the Characterization of High Level Waste Glasses," Pacific Northwest Laboratory Report BNWL-2252, June 1977.

98. A. R. Hall, J. T. Dalton, B. Hudson and J. A. C. Marples, "Development and Radiation Stability of Glasses for Highly Radioactive Wastes,"in Management of Radioactive Wastes From the Nuclear Fuel Cycle, 2, (IAEA, Vienna, 1976) p. 3. Available from the IAEA, Kartner Ring II, Box 590, A-101b, Vienna, Austria.

99. M Antonini, F. Lanza, and A. Manara, "Simulations of Radiation Damage in Glass," in Ceramics in Nuclear Waste Management, USDOE Conference Proceedings CONF 790420, May 1979, p. 289.

100. F. W. Clinard, Jr. and G. F. Hurley, "Effects of Irradiation on Structural Properties of Crystalline Ceramics," in Ceramics in Nuclear Waste Management, USDOE Conference Proceedings CONF-790420, May 1979, p. 300.

101. R. F. Haaker and R. C. Ewing, "The Metamict State Radiation Damage in Crystalline Materials," in Ceramics in Nuclear Waste Management, USDOE Conference Proceedings CONF-790420, May 1979, p. 310.

102. W. Primak, "Notes on Radiation Effects on Glasses Pertinent to Solid Storage of Radioactive Wastes," in Ceramic and Glass Radioactive Waste Forms, USERDA Conference Proceedings CONF 770102, 1977, p. 157.

103. K. Scheffler and U. Reige, Kernforschungszentrum Karlsruhe, "Investigation on the Long Term Radiation Stability of Borosillicate Glasses Against Alpha-Emitters," Kernforschungzentum Karlruhe (F.R.G.) Report, Report No. KFK 2422, (April 1977). Available from Gesellschaff fur Kernsforshung M.B.H., Karlsruhe, W. Germany.

104. W. J. Weber, R. P. Turcotte, L. R. Bunnell, F. P. Roberts and J. H. Westsik, Jr., "Radiation Effects in Vitreous and Devitrified Simulated Waste Glass," in Ceramics in Nuclear Waste Management,USDOE Conference Proceedings CONF-790420, May 1979, p. 294.

105. N. E. Bibler and J. A. Kelley, "Effect of Internal Alpha Radiation on Borosillicate Glass Containing Savannah River Plant Waste," Savannah River Laboratory Report, DP-1481, May 1978.

106. F. P. Roberts, G. H. Jenks, and C. D. Bopp, Pacific Northwest Laboratory, "Radiation Effects in Solidifed High-Level Wastes Part I, Stored Energy," Pacific Northwest Laboratory Report BNWL 1944, January 1976.

107. K. D. Reeve, D. M. Levins, E. J. Ramm, J. W. Wolfreg, W. J. Buyk and R. K. Ryan, "Progress in SYNROC Technology at Lucas Heights," Presented by C. J. Hardy at Waste Management '80 -The State of Waste Disposal Technology, Mill Tailings and Risk Analysis Models, Symposium Sponsored by the University of Arizona and the U.S. DOE, Tuscon, AZ, March 10-14, 1980, (Proceedings in press).

108. J. C. Dran, V. Langevin, M. Maurette, and J. C. Petit, "A Microscopic Approach for the Simulation of Radioactive Waste Storage in Glass," in Scientific Basis for Nuclear Waste Management, Vol. II, C. M. Northrop Jr., Ed. (Plenum Press, N.Y., 1980), p. 135-140.

109. J. C. Dran, M. Maurette and J. C. Petit, "Radioactive Waste Storage Materials: Their Alpha Recoil Aging," Science 209, 1518-19 (1980).

110. J. C. Dran, M. Maurette, B. V. Assent and J. C. Petit, "Ion Implantation Effect on the Leach Resistance of Glasses and Minerals: Implications for Radioactive Waste Storage," Abstracts, Symposium D; Scientific Basis for Nuclear Waste Management, Annual Meeting, Materials Research Society, Boston, November, 1980.

111. E. H. Hirsch, "A New Irradiation Effect and its Implications for the Disposal of High-Level Radioactive Waste," Science, 209, 1520-22.

112. A. E. Ringwood, Safe Disposal of High Level Nuclear Reactor Wastes: A New Strategy, Australian National University Press, Canberra, Australia and Norwalk, Ct., USA, 1978.

113. K. D. Reeve and J. L. Woolfrey, "Accelerated Irradiation Testing of SYNROC Using Fast Neutrons - I. First Results on Barium Hollandite, Perovskite and Undoped SYNROC B," J Austr. Ceram. Soc. 16, pp. , 1980.

114. F. P. Roberts, R. P. Turcotte and W. J. Weber, Pacific Northwest Laboratory, "Materials Characterization Center Workshop on the Irradiation Effecs in Nuclear Waste Forms - Summary Report," Pacific Northwest Laboratory Report PNL 3588/UC-70, 1981.

115. Panel on Waste Solidification (Rustum Roy, Chairman), National Academy of Sciences, "Solidification of High Level Radioactive Wastes," USNRC Report NUREG/CR-0895, p. 168.

116. G. Das and T. E. Mitchell, "Electron Radiation Damage in Quartz," Radiation Effects 23, 49 (1972).

117. W. Primak and R. Kampworth, "The Radiation Compaction of Vitreous Silica," J. Appl. Phys. 39, 5651 (1968).

118. J. E. Shelby, "Effect of Radiation on the Physical Properties of Borosilicate Glasses," J. Appl. Phys. 51, 2561-65, 1980.

119. L .W. Hobbs, "Radiation Effects in Analysis of Inorganic Specimens by TEM," in Introduction to Analytical Electron Microscopy, eds. J. J. Hren, J. T. Goldstein, and D. C. Joy, eds. (Plenum Press, New York, 1979) p. 437.

120. L. W. Hobbs, "Application of Transmission Electron Microscopy to Radiation Damage in Ceramics," J. Am. Ceram. Soc. 62, 267-278, 1979.

121. L. W. Hobbs, "Point Defect Stabilization in Ionic Crystals at High Defect Concentrations," J. Physique Colloq. 37: C7-3, 1976.

122. K. J. Swyler, R. W. Klaffky and P. W. Levy, "Recent Studies on Radiation Damage Formation in Synthetic NaCl and Natural Rock Salt for Radioactive Waste Disposal Applications," in Scientific Basis for Radioactive Waste Management, Vol. II, C. J. Northrop, Jr., Ed. (Plenum Press, N.Y. 1980), pp. 553-560.

123. U. Jain and A. B. Lidiard, "The Growth of Colloidal Centres in Irradiated Alkali Halides," Phil. Mag. 35, 245, 1977.

124. J. S. Stroud, "Color Centers in a Cerium Containing Silicate Glass," J. Chem. Phys. 37, 836-841, 1962.

125. P. W. Levy, P. L. Mattern and K. Lengweiler, "Studies on Nonmetals During Irradiation: The Growth and Decay of F Centers in KCl at 20°C," Phys. Rev. Lett. 24, 13-16, 1970.

126. W. Primak, "Postirradiation Alkali Migration," J. Electrochem. Soc. 127, 1002, 1975.

127. I. V. Draganic and Z. D. Draganic, The Radiation Chemistry of Water, Academic Press, New York, 1971.

128. G. H. Jenks, Oak Ridge National Laboratory, "Review of Information on the Radiation Chemistry of Materials Around Waste Canisters in Salt and Assessment of the Need for Additional Experimental Information," Oak Ridge National Laboratory Report ORNL 5607, March 1980.

129. W. G. Burnes and P. B. Moore, "Water Radiolysis and its Effect Upon In-reactor Zircaloy Corrosion," Radiation Effects 30, 233, 1976.

130. E. R. Vance and K. K. S. Pillay, Pennsylvania State University, "Structural Damage From Fission Fragment Irradiation in Crystalline Nuclear Waste Phases," DOE Subcontractor Report DOE/ET/41900-5, 1980.

131. D. D. Walker, M. D. Dukes, M. J. Plodinec and N. E. Bibler, "Effect of Radiation on Leaching of Borosilicate Glass Containing Defense High-

Level Nuclear Waste," Abstracts, Symposium on Chemical Consideration for Important Radioactive Waste Species, 181st National Meeting of the American Chemical Society, Atlanta, March 1981.

132. W. J. Weber, J. W. Wald, and W. J. Gray, "Radiation Effects in Crystalline High-Level Nuclear Waste Solids," Abstracts-Symposium D: Scientific Basis for Nuclear Waste Management, Annual Meeting, Materials Research Society, Boston, November 1980.

133. W. J. Weber, Pacific Northwest Laboratory, "Ingrowth of Lattice Defects in Alpha-Irradiated UO_2 Single Crystals," Pacific Northwest Laboratory Report PNL-SA-8574, August 1980. (To appear in J. Nuclear Materials.)

134. L. Cartz, F. G. Karioris, R. E. Fournelle, A. Gowda, K. Ramasami, and M. Limoges, "Metamictization by Heavy Ion Bombardment of Alpha-Quartz, Zircon, Momazite and Nitride Structures," Abstracts-Symposium D: Scientific Basis for Nuclear Waste Management, Annual Meeting, Materials Research Society, Boston, November 1980.

135. R. P. Turcotte, "Radiation Effects in Solidified High Level Waste, Part 2, Helium Behavior," Pacific Northwest Laboratories Report BNWL-2051, May 1976.

136. G. Malow and H. Andersen, "Helium Formation From Alpha Decay and Its Significance for Radioactive Waste Glasses," in Scientific Basis for Nuclear Waste Management, Vol. I, G. J. McCarthy, Ed. (Plenum Press, New York, 1979), pp. 109-115.

137. J. E. Mendel, "The Storage and Disposal of Radioactive Waste as Glass in Canisters," Pacific Northwest Laboratory Report, PNL-2764., 1978.

138. D. M. Martin, Iowa State University, "Thermal Stresses in Waste-Disposal Systems - Annual Report for the Period Ending 30 September, 1979," NRC Contractor Report NRC-04-78-268, 1980.

139. M. Antonini, P. Camagni, F. Lanza and A. Manara, "Atomic Displacements and Radiation Damage in Glasses Incorporating HLW," in Ceramics in Nuclear Waste Management, USDOE Conference Proceedings CONF-790420, May, 1979, pp. 127.

140. J. M. Rusin, W. J. Gray, and J. W. Wald, "Multibarrier Waste Forms, Part II: Characterization and Evaluation," Pacific Northwest Laboratories Report NL-2668-2, August, 1979.

141. N. E. Bibler, "Radiolytic Gas Prodution From Concrete Containing Savannah River Plant Waste," Savannah River Laboratory Report DP-1464, January 1978.

142. S. Katz, "The Reaction of Hydrogen and Oxygen in the Presence of Concretes Incorporating Simulated Radioactive Waste," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. M. Northrop Jr., Ed. Plenum Press, New York 1980; pp. 577-584.

143. P. V. Murphy and B. Gross, "Polarization of Dielectrics by Nuclear Radiation II: Gamma-Ray-Induced Polarization," J. Appl. Phys. 35 171, (1961).

144. T. D. Chikalla, et al., "Radiation Effects," p. 243 in Ceramic and Glass Radioactive Waste Forms, USERDA Conference Proceedings CONF-770102, 1977, pp.243.

145. American Physical Society Study Group on Nuclear Fuel Cycles and Waste Management (L. C. Hebel, Chairman), "Report to the American Physical Society," Rev. Mod. Phys 50, S130 (1978).

146. P. H. Permar, and W. R. McDonell, "Significance of Radiation Effects in Solid Radioactive Waste," in ASTM Proceedings 10th Symposium on Effects of Radiation on Materials, ASTM STP-000 1980.

147. D. W. Kneff, "Radiation Effects Simulation in High Level Nuclear Waste Forms: A Literature Review," Supporting Document No. 364TI000001, Energy Systems Group, Rockwell International, Canoga Park, California, 1980.

148. H. M. Lee, "Natural Radiation Damage in Solids: A Literature Review," Supporting Document No. 364TI000001, Energy Systems Group, Rockwell International, Canoga Park, California, 1980.

149. Materials Characterization Center, Pacific Northwest Laboratory, "Draft - Materials Characterization Center MCC-6 Alpha-Decay Effects in Radioactive Waste Forms Test," December 1980.

150. K. J. Swyler to E. Wick, Appendix 6, BNL Monthly Management Report on NRC Contract Fin A-3158, November 1980.

151. R. P. Turcotte, Pacific Northwest Laboratory, to K. J. Swyler, Brookhaven National Laboratory, Private Communication, January 14, 1981.

152. W. R. McDonnel and N. E. Bibler, Savannah River Laboratory to K. J. Swyler, Brookhaven National Laboratory, Private Communication, May 7, 1981.

153. K. Kigoshi, "Alpha-Recoil Thorium-234: Dissolution into Water and the Uranium-1234/Uranium-238 Disequilibrium in Nature," Science 173, 47, 1971.

154. R. L. Fleischer, "Isotope Disequilibrium of Uranium: Alpha Recoil Damage and Preferential Solution Effects," Science 207, 979 (1980).

155. R. L. Fleisher and P. B. Price, "Charged Particle Tracks in Glass," J. Appl. Phys. 34, 2903 (1963).

156. R. F. Haaker and R. C. Ewing, "Differential Thermal Analysis of Some Irradiated Materials: Discussion," Am. Mineral. 64, 1131-32, (1979).

157. R. P. Turcotte, J. W. Wald and R. P. May, "Devitrification of Nuclear Waste Glasses," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. M. Northrop, Jr., Ed. Plenum Press, New York, 1980, pp. 141-146.

158. A. N. Goland, "Radiation Damage of Non-Metallic Solids," in Radiation Damage in Metals, H. L. Peterson and S. D. Harkness, Eds., (American Society for Metals, Metals Park, Ohio, 1976) pp. 366-393.

159. G. W. Arnold, G. B. Krefft, and C. B. Morris, "Atomic Displacement and Ionization Effects on the Optical Absorption and Structural Properties of Ion-Implanted AL_2O_3," Applied Phys. Lett. 25, 540, 1974.

160. T. M. Ahn and K. J. Swyler, "An Analysis of Radiation-Induced Stresses in High-Level Waste (Draft)," Appendix 3, BNL Monthly Management Report on NRC Contract FIN-A-3158, February 1981.

161. R. L. Fleischer, P. B. Price and R. M. Walker, Nuclear Tracks in Solids, University of California Press, Berkeley, Calif. 1975.

5. TESTING OF THE WASTE CONTAINER

This chapter describes testing of the waste container from the standpoints of corrosion, mechanical effects and radiation effects.

5.1 Corrosion Testing

5.1.1 Introduction

A waste package must demonstrate compliance with proposed licensing criteria before it can be put into use. Such a demonstration will involve extensive testing and evaluation. The container must have several basic requirements in order to meet the criterion of containment for 1,000 years, as currently proposed by the NRC. These requirements were recently reviewed by Scott[1]. Based on available data, it is anticipated that the container will be the principal means for meeting the 1,000 year containment criterion.

Recent papers[2,3] have indicated that container materials are now available which may satisfy this criterion. Research in Sweden[2] indicated that either copper or lead can withstand the groundwater environment in igneous rock for periods of a thousand years or more. Results from tests performed at Sandia[3] indicate that a titanium alloy (Ticode 12 0.8% Ni, 0.3% Mo, Bal. Ti) could withstand attack by some brine solutions for 300-600 years.

Corrosion testing is the principal area of concern in evaluating the performance of potential container materials. The time at which the container is breached will determine the onset of waste form leaching, and the migration of radionuclides into the backfill.

Specifically, the purpose of corrosion testing of candidate container material will be twofold. Laboratory tests will be used to select the most suitable material by predicting the service life of a container for the worst possible conditions in the repository. Also, the mechanism of corrosion will be studied to justify that prediction. In this section corrosion testing procedures concerning HLW management will be discussed, present corrosion testing efforts of DOE and BNL will be reviewed, and recommendations will be made. Radiation effects on corrosion of metals will be discussed separately in Section 5.3.

5.1.2 Types of Corrosion

Fontana[4] classified metallic corrosion into eight types that cover practially all corrosion failures and problems. The eight types are:

(1) Uniform, or general attack

(2) Galvanic, or two-metal corrosion,

(3) Crevice corrosion,

(4) Pitting,

(5) Intergranular corrosion,

(6) Selective leaching,

(7) Erosion corrosion, and

(8) Stress corrosion.

Hydrogen attack may be added to the list.

Under nuclear waste repository conditions, most of these corrosion types, except erosion corrosion, are possible. However, three types of corrosion, i.e., galvanic corrosion, intergranular corrosion and selective leaching can be avoided by proper materials selection. Thus, corrosion studies for a HLW metallic container should be focused on uniform corrosion, crevice corrosion, pitting corrosion, stress corrosion and hydrogen effects.

The purpose of this section is to identify the types of corrosion tests required, to review the state of knowledge concerning the tests and to make recommendations concerning specific test methods and research necessary.

5.1.3 Test Variables

In a recent publication[5], Braithwaite and Molecke discussed the variables which can have an effect on container corrosion in a waste repository. They list some environmental parameters for various repositories, (Table 5.1), and discuss the effect of these variables as follows:

5.1.3.1 Temperature

Increases in temperature generally increase the corrosion rates of metals.[6,7] However, as Shannon[8] noted for steel in geothermal brines, the corrosion retardant passivating film formed sometimes becomes more protective as temperature is increased and the observed corrosion rates decrease. Also, increases in temperature in an open system will cause a depletion in dissolved oxygen in aqueous solutions. This will decrease the corrosion rate of metals whose rate is controlled by diffusion of oxygen (for example, 1018 mild steel).

5.1.3.2 Pressure

The restraining pressure to which an HLW canister is subjected in a waste repository affects the corrosion rate primarily because it influences the physical state of intruding water and the concentration of dissolved gaseous species. The lithostatic (rock overburden) pressure, combined with low gas permeability, in a bedded salt repository, or the hydrostatic pressure in the deep ocean sediment, will prevent water vaporization even at high waste temperatues. HLW emplaced in hardrock formations will not be exposed to liquid

water because of the lack of a confining pressure. These arguments, of course, depend upon the sealing and reflux properties of the formations.

Table 5.1

Repository Isolation Environments for High-Level Waste[5]

Geologic Formation and Waste Type	Maximum Interface Temperature	Lithostatic/ Hydrostatic Pressure	Chemistry
Bedded Salt:			
Spent fuel	70-100°C	18 MPa	Dry NaCl
Defense HLW	70-100°C	18 MPa	Dry NaCl
Reprocessed HLW	250°C[a]	18 MPa	Dry 98% NaCl, with dispersed 1/2% H_2O
Reprocessed HLW	150°C[a]	18 MPa	With potential inundation due to localized intrusion of NaCl-$MgCl_2$ brine or hydrologic flow
Subseabed Sediments:			
Reprocessed HLW	200°C	55 MPa	Seawater saturated sediments (40% solids)
Basalt, Shale, Tuff:			
Reprocessed HLW	250-300°C	Atmospheric	Air and steam for about 100 years, then possibly inundated with ground water

[a]Assumes 37 watts/m^2(150 kW/acre) container spacing in repository: does not include radiolysis effects.

5.1.3.3 Solution Chemistry

Waste containers will be exposed to any thermal decomposition products of the geologic isolation formation (CO, SO_2, etc.) and any dissolved and gaseous species present (O_2, N_2, CH_4, H_2, etc.). In general, species in solution which increase the oxidizing power of that solution (O_2, H^+, H_2S, NO_3, etc.) will increase the corrosion rate. Hydrogen ions can also reduce the thickness and therefore the effectiveness of a metal's passivating layer.[6] Basic pH conditions can cause caustic stress corrosion cracking or even rapid dissolution if the metal is amphoteric.[6] Chloride ion is potentially the most aggresive of the ions because it promotes localized passive film breakdown (which leads to pitting), and is a key constituent in causing stress corrosion cracking of many alloys. Large concentrations of chloride can inhibit the corrosion rates of many alloys by salting out dissolved oxygen and/or by adsorbing and blocking many active surface sites.[6]

5.1.3.4 Stress

The tensile stress present in the container wall is one of the essential requirements for stress corrosion cracking in geologic isolation conditions. For the candidate alloys an environment-specific experimental study needs to be conducted. For susceptible alloys, the threshold tensile stess depends strongly on temperature, solution composition, and the presence of an aqueous phase.

5.1.3.5 Sensitization and Welding

Alloys containing carbon and chromium can be susceptible to sensitization. For example, sensitization in stainless steels refers to the thermally induced formation of chromium carbide at or near grain boundaries. This increases the susceptibility of the alloy to intergranular attack and intergranular stress corrosion cracking.[6,7] Welding, because of the high temperatures involved, often leads to sensitization and tensile stress in welded regions. Stainless steel 304, for example, undergoes sensitization at temperatures above 400°C.

5.1.4 Test Specimens and Equipment

Specimens used in the corrosion tests should be representative of the materials to be used for the containers. That is, the coupons should be wrought, cast, etc., if that is the form to be used in container fabrication, and be subjected to similar heat treatments and surface finishes. In these tests, the corrosion rates are expected to be very small, so that it may be necessary to polish the surfaces in order to detect corrosion in the surface layers. However, the effect of surface polishing on the measured corrosion rates and process should be evaluated. If welds are to be used in container fabrication, their corrosion resistance must be evaluated because of the significant structural changes (cast structure, heat affected zone, etc.) produced by welding.

For laboratory testing, conventional specimens can be used. General corrosion, pitting, and crevice corrosion can be determined on specimens of almost any geometry, determined by the test being performed and equipment used. Some tests such as stress corrosion tests (e.g., U-bend tests, fracture mechanics tests and slow strain rate tests) require specially shaped specimens shown in Figures 5.1 and 5.2. Specimens should always be made in standard shapes and from well characterized materials (fabrication history, composition, heat treatment, etc.).

Corrosion test apparatus can be glass or metallic vessels containing the specimen, or autoclaves (for normal or high pressures) which are sometimes modified to perform special tests. The apparatus used is largely governed by the test temperature and aggressiveness of the test environment. A simple resin flask recommended for immersion testing in ASTM G31 is shown in Figure 5.3. Whatever apparatus is used, its geometric configuration and construction materials should not interfere with the corrosion test results.

5.1.5 Analytical Methods for Corrosion Testing

Traditionally, corrosion testing laboratories have avoided the use of analytical chemistry to characterize solution and solid corrosion products formed during testing. With increased emphasis on the determination of corrosion mechanisms, more chemical and physical techniques will be required to characterize the entire corrosion system. Most of the same analytical techniques and methods described for leach testing (Chapter 4, Section 4.2.3) are equally applicable to corrosion testing, although the required detection and resolution performance are unlikely to be as demanding with container materials.

Corrosion products in testing solutions can be analyzed by Atomic Absorption Spectrophotometery or Inductively Coupled Plasma Spectroscopy. Solid corrosion products on surfaces have been most often characterized using Scanning Electron Microscopy and Energy Dispersive X-ray Analysis (SEM-EDX). More recently, Scanning Auger Microscopy (SAM) has provided much higher spacial resolution, both in lateral and depthwise directions. This technique should be particularly valuable for detection of localized products associated with pitting or crevice corrosion.

5.1.6 Accelerated Testing and Extrapolation of Data

Corrosion testing can be considered in two categories - accelerated tests and non-accelerated tests. In situ tests may be included in the latter category.

Valid accelerated corrosion tests are a necessity for assessing the service life of very corrosion resistant materials. However, it should be clear that the results from accelerated tests do not always yield usable data to design. Accurate service life can be predicted only if accelerated test results can be correlated with actual corrosion behavior.

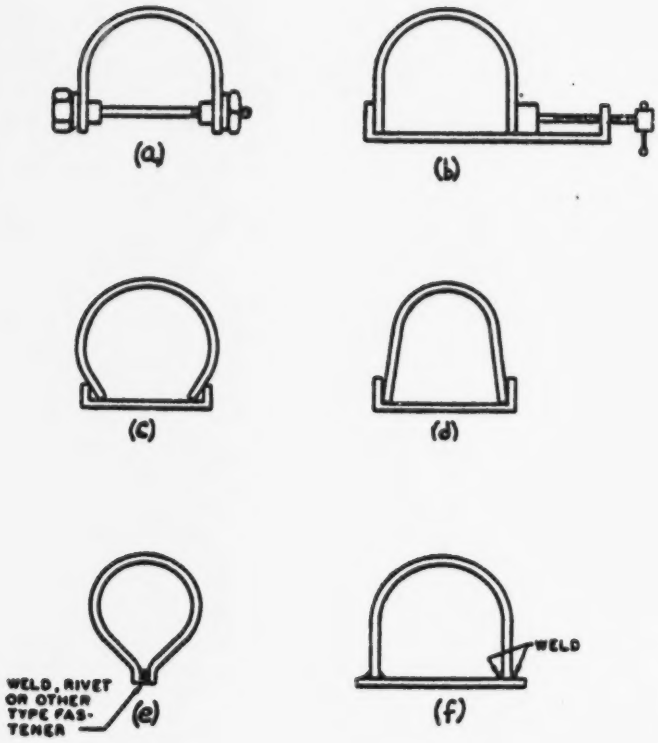

Figure 5.1 Typical stressed U-bends.

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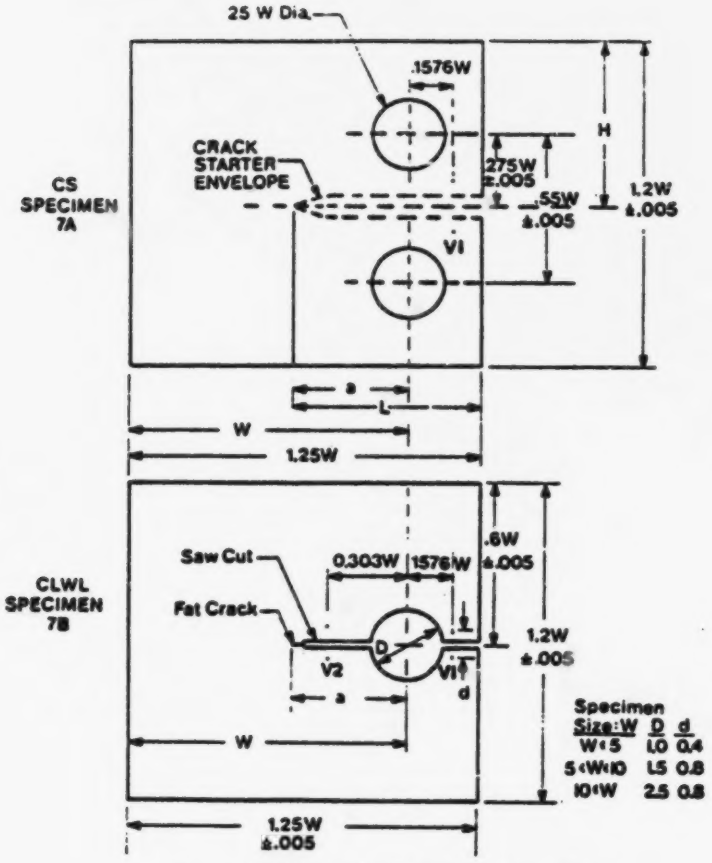
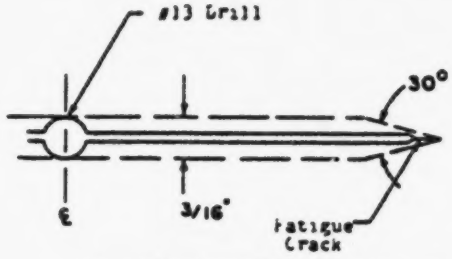


Compact and Crack-Line-Wedge-Loaded Specimens.



Enlarged View of the Right Half of the Permitted Notch Envelope in CCT Panels.

Figure 5.2 ASTM specifications for compact and crack-line-wedge-loaded specimens (ASTM E561).

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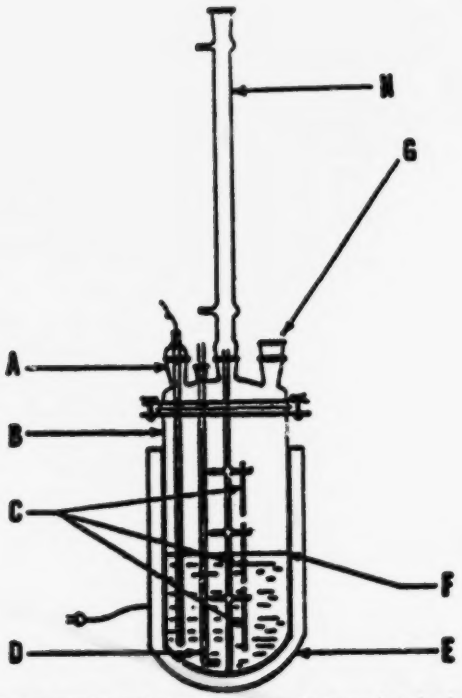

NOTE—The flask can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of top to flask is such that more sophisticated apparatus can be added as required by the specific test being conducted. *A* = thermowell, *B* = resin flask, *C* = specimens hung on supporting device, *D* = air inlet, *E* = heating mantle, *F* = liquid interface, *G* = opening in flask for additional apparatus that may be required, and *H* = reflux condenser.

Figure 5.3 Typical resin flask (ASTM 631).

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There may be two ways to make use of the accelerated test results. The first one is extrapolating the accelerated test results directly to 1000 yr time frames assuming that the accelerated test is an overestimate. If this assumption can be justified, and if the extrapolation gives an estimated service life that meets waste package criteria, this method will be acceptable. The second way is extrapolating the accelerated test results to non-accelerated conditions, and then extrapolating the estimated actual corrosion rate to extended times. This involves two extrapolations, which requires justification.

An important consideration in extrapolating corrosion data is the nature of the corrosive attack. If the corrosion is uniform in nature, the extrapolation to some finite time is relatively simple. However, in the case of localized attack, such as pitting, crevice corrosion, intergranular or stress corrosion, extrapolation is extremely difficult since the initiation time and penetration rates for these corrosion types are difficult to determine. For applications such as waste containers, it would be best to select materials which do not exhibit these types of corrosion.

General experimental variations are used to accelerate corrosion testing, namely increasing the temperature, increasing the corrosiveness of the solution, increasing stress intensity or applying potential. Radiation dose may be added to this list. These variations can be used in combinations.

Extrapolation of the results from accelerated tests to expected repository conditions should be justified even for the simplest corrosion type, such as uniform corrosion. For example, to check the validity of temperature acceleration, the data should include a significant number of different temperatures. When plotted, the test results should give a linear Arrhenius plot. Results deviating from linearity should be investigated for a possible change in the corrosion mechanism. A mechanism change with increased temperature would invalidate the acceleration tests.

Ideally, both accelerated and non-accelerated tests should be conducted simultaneously and great care should be given to the reproducibility. The complex nature of most corrosion mechanisms makes it difficult to obtain acceptable reproducibility, therefore requiring multiple testing using "identical" specimens.

5.1.7 Standardized Test Procedures

One of the problems encountered where laboratory tests are conducted by several laboratories is the difficulty in comparing results, due to non-uniformity in materials, test apparatus, and procedures used. Such problems usually occur early in a testing program and are not resolved until after a great expenditure of time and funds. There are, however, standard test procedures which have been developed to circumvent this problem. The ASTM has adopted many standards for corrosion testing, some of which are:

ASTM G1 - Preparing, cleaning, and evaluating corrosion test specimens.

ASTM G3 - Conventions applicable to electrochemical measurements in corrosion testing.

ASTM G5 - Standard reference method for making potentiostatic and potentiodynamic anodic polarization measurements.

ASTM G28 - Detecting susceptibility to intergranular attack in wrought nickel-rich, chromium bearing alloys.

ASTM G30 - Making and using U-bend stress corrosion test specimens.

ASTM G36 - Performing stress corrosion cracking tests in a boiling magnesium chloride solution.

ASTM G41 - Determining cracking susceptibility of titanium alloys exposed under stress to a hot salt environment.

ASTM G46 - Examination and evaluation of pitting corrosion.

These specifications are quite complete. For example, a sketch showing stressed U-Bends (ASTM G30) is shown in Figure 5.1, and the definitions of pit corrosion types are shown in Figure 5.4, (ASTM G46). Other organizations having corrosion standards are the National Association of Corrosion Engineers (NACE) and the International Atomic Energy Agency (IAEA).

5.1.8 MCC Workshop on Corrosion of Engineered Barriers

In August 1980 MCC organized a workshop on corrosion of container metals. An excellent review of the existing corrosion test methods was produced and hierarchies of tests for each form of corrosion were generated. BNL agrees with most of the conclusions and recommendations made. The following subsections are quoted from the MCC Summary Report of the workshop on Corrosion of Engineered Barriers.[10]

5.1.8.1 Uniform Corrosion

A hierarchy of test procedures to obtain data on corrosion penetration for various environments was developed. The approach discussed is one in which non-accelerated and accelerated tests are necessary to qualify corrosion-rate data for extrapolation to 1000-yr service. Accelerated tests--defined as tests where the extent of corrosion attack is increased for a given test duration by manipulation of radiation intensity, temperature, or chemistry--are required both to aid in interpretation of data obtained in non-accelerated tests and to provide a basis for extrapolation of data to times beyond practical test durations.

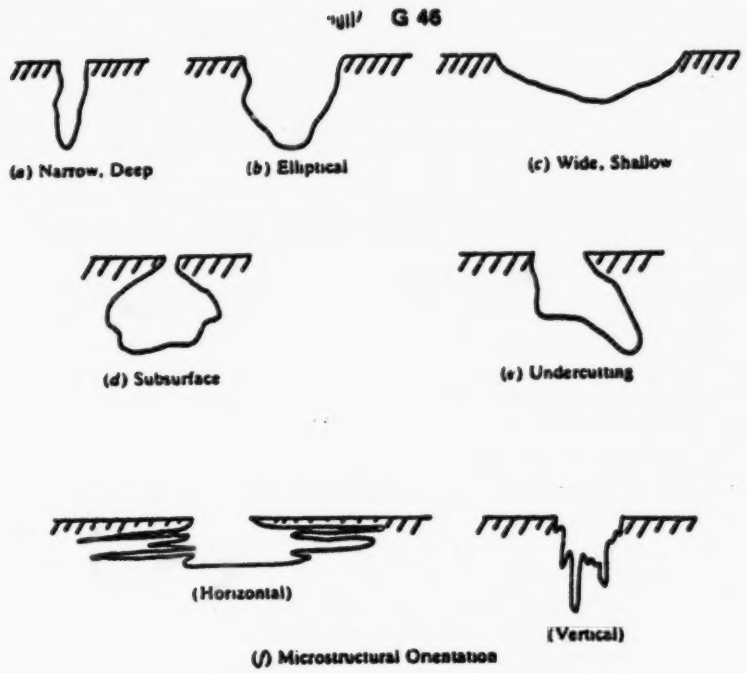

Figure 5.4 Variations in the cross-sectional shape of pits (ASTM G-46).

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Uniform corrosion rate data (i.e., weight change) will be obtained for the temperatures, solutions, and radiation conditions expected in repositories and will, if possible, provide the primary basis for lifetime predictions. In some cases, low corrosion rates may be difficult to quantify (e.g., at low temperatures or for alloys such as titanium). In these cases, accelerated testing will be useful for obtaining quantitative data consistent with the non-accelerated test results.

In all cases, the corrosion behavior at times beyond the test duration can be confidently predicted only if the corrosion behavior is characterized by additional accelerated tests. Results from accelerated tests should support corrosion rate data from non-accelerated tests.

Evaluation techniques were discussed and ranked with respect to their usefulness in establishing the relevance of both non-accelerated and accelerated test techniques to 1000-yr extrapolation. The gravimetric test, polarization resistance, and surface analysis for film thickness were the techniques best suited for predicting materials performance. The gravimetric test was considered sufficient for screening.

5.1.8.2 Non-uniform Corrosion

Three corrosion modes received attention: pitting, crevice corrosion, and intergranular corrosion. The only one for which there is an established, though tenuous, basis for extrapolation of data to 1000-yr service is pitting corrosion. MCC is considering the application of Extreme-value Theory[11] of pitting to predict service life. Crevice corrosion and intergranular corrosion have not received similar attention. Documenting the absence of or minimizing crevice and intergranular corrosion appears to be the current recourse to solving the problem because no quantitative, predictive laws are known to be applicable to these corrosion modes. Test methods to document the absence of these two corrosion modes were discussed and are presented. It was emphasized that design and fabrication practices must be carefully chosen to avoid or minimize crevice and intergranular corrosion in alloys that are susceptible to these two corrosion modes.

5.1.8.3 Stress-Corrosion Cracking

There are defined techniques for evaluating the susceptibility of metals to stress-corrosion cracking (SCC). A combination of smooth-bar and precracked specimens was recommended to assess SCC resistance of materials. Predicting the service life of a material that exhibits SCC is the most difficult problem. If this is required--i.e., if materials susceptible to SCC are used--then threshold stress intensity most conservatively obtained from cyclically loaded specimens was considered the best parameter for design purposes. The C-ring test, U-bend test, and constant-extension-rate test (CERT) were recommended as screening tests to document the absence of SCC. Accelerated tests, based on increasing severity of environment, were also recommended. The CERT test was considered especially useful for accelerated testing for the purpose of screening.

5.1.8.4 Hydrogen Effects

Hydrogen effects were discussed and static and dynamic test techniques were recommended. Hydrogen effects are difficult to detect and predict, especially with respect to long-time service, so it is unlikely that a large number of materials will ever be screened based on susceptibility to hydrogen embrittlement. Avoidance of hydrogen-related failure in barriers is best assured by obtaining the failure predictive parameters, K_{Th} and J_{Th} and using the materials within the stress/flaw values corresponding to these threshold parameters.

5.1.8.5 Proposed MCC Test Procedures

The following are the first corrosion test procedures that will be developed by the MCC. These procedures were not presented explicitly at the workshop. Since the workshop these five test procedures were identified for submittal to the MRB. Additional procedures will be developed as repository conditions are further defined.

These tests will address the failure modes of uniform corrosion, pitting, crevice corrosion, stress-corrosion cracking, and hydrogen effects. Many evaluation techniques are necessary and will be incorporated into these procedures.

MCC-B1 Static Immersion Corrosion Test

The procedure will determine weight change in solutions of brine, simulated basalt ground water, and a tuff-related ground water. Evaluation will include observations on pitting, which will require large specimens. The procedure will accommodate autoclave testing.

MCC-B2 Flow Immersion Corrosion Test

This test is nearly identical to MCC-B1 except that a flowing test environment will be specified.

MCC-B3 Stress-Corrosion Screening Test

This test will use U-bend and C-ring specimens to screen candidate materials. CERT will be optional.

MCC-B4 Stress-Corrosion Threshold Test

This test will determine K_{Th} for crack propagation in various environments under cyclic stress conditions. Pressurized tests will be included.

MCC-B5 Radiation-Environment Corrosion Test

This test will determine weight changes in pressurized aqueous environments with a gamma radiation field. Other possible chemical effects,

such as hydrogen pickup will be determined. Observations on pitting and crevice corrosion will be correlated with results from MCC-B1 and MCC-B2.

5.1.9 Test Procedures used by DOE Contractors

5.1.9.1 Sandia National Laboratory

Since 1976, Sandia has investigated the corrosion behavior of candidate alloys for use as high-level waste containers or overpacks. Figure 5.5 shows one of the engineered barrier concepts which utilize an overpack. In this design, the HLW container is assumed to be made of a relatively inexpensive material that provides mechanical properties. The function of the overpack is corrosion resistance, not support strength.[12] Test procedures used by Sandia are reviewed below:

(a) Screening Test [5]

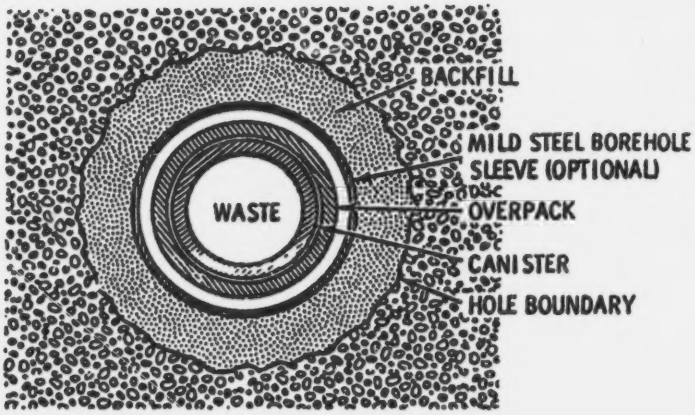
The high-temperature hydrothermal experiments were conducted for periods of two weeks to six months in SS-316 or Hastelloy C-276 autoclaves. Three different environments were used, two different brine compositions and seawater. The corrosion specimens (1.2 cm x 1.2 cm x 0.62 cm) were sealed in either Pyrex or fused quartz tubes along with an aliquot of solution (deep sea-sediments and crushed bedded salt were added to seawater and brine experiments, respectively). The experiments with oxygen were conducted in open ended fused quartz tubes. At the completion of the experiments, corrosion products were removed by glass bead surface peening and the corrosion rate calculated from weight loss measurements.

The effect of temperature on the initial corrosion rate of 1018 mild steel in deoxygenated seawater and brine was determined using linear and Tafel DC electrochemical polarization techniques, in the temperature range of 25-200°C. These rates were an order of magnitude higher than measured from long-term loss results. This is because the electrochemical derived value represents an instantaneous initial rate. Over 20 metals were tested, and a titanium alloy, Ticode-12 was selected as a prime candidate for further detailed testing. Ti-50A is considered as a possible backup material in applications where temperatures are less than about 100°C.

(b) Titanium Alloy Corrosion [3]

(i) Uniform Corrosion

Braithwaite et al.,[5] studied the general corrosion resistance of titanium alloys in hot brines at 250°C. Titanium specimens were exposed to hot brines in a static mode, in a standard 1 liter autoclave constructed from Hastelloy C-276. Loose fitting Hastelloy C-276 or PTFE teflon liners were also employed in an attempt to protect the autoclaves from unanticipated corrosion problems. The titanium corrosion coupons, and 2.4 mm diameter wire of the alloy of interest, were used for coupon test and electrochemical measurements, respectively. For electrochemical measurements, a silver-silver chloride internal reference electrode filled with 0.1 N KCl was used.



- Number of engineered barriers, exclusive of waste form: 3 (canister, overpack, backfill)
- Materials for overpack: Ti-base, Zr-base alloys; Ni-Cr, Fe-Cr alloys; ceramics; graphite
- Materials for canister: Cu, Cu-base alloys; Fe-base, Ni-base alloys
- Emplacement procedure: Overpacked canister placed in sleeved borehole. If borehole is not sleeved, overpacked canister is placed in borehole, backfill then added. Note that the borehole sleeve is not considered a barrier in this concept.

Figure 5.5 Engineered barrier system compatible with both oxidizing and reducing environments. The overpack is resistant to oxidizing conditions, and the canister resistant to reducing conditions (Ref. 13).

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Uniform corrosion rates were calculated using conventional weight gain and solution analysis techniques. To aid in this determination, oxide layer thickness and compositional profile measurements were made on selected samples utilizing ion backscattering analysis.

(ii) Nonuniform Corrosion

Crevice corrosion susceptibility was studied by placing the mirror polished surface of one coupon on top of another polished specimen. Test temperature was 250°C.

(iii) Stress Corrosion Cracking

Braithwaite et al.[5], used a slow strain rate test and a fracture mechanics technique to study stress corrosion cracking at 250°C. The slow strain rate tests were conducted inside Hastelloy C-276 autoclaves with internal structures also constructed of Hastelloy C-276. PTFE teflon was used to seal all feedthroughs, which were of a modified Conax type. In addition, ceramic (Al_2O_3) cylinders were used around the load pins to isolate the test specimen electrically. The fracture mechanics specimens, (compact tension geometry), were tested using the constant displacement technique. A heavy load-ring, which has bolt mounted clevises across its diameter, was used to load the specimen to a predetermined stress intensity in the test environment. The specimen was electrically isolated from the crevices with insulated load pins. The fracture mechanics specimens were fatigue precracked over a stress intensity range of 2 to 11 MN/m^2 and exposed to the environment prior to loading.

(iv) Hydrogen Effects

Sandia has planned to evaluate the effects of hydrogen absorption, if any, on the mechanical properties of titanium alloys in FY81. Measurements to be made include critical hydrogen concentrations necessary to affect tensile loading, slow strain rates, and hydride formation.

5.1.9.2 Pacific Northwest Laboratory

(a) Screening Test[14]

PNL conducted the screening studies with specimens primarily in U-bend configurations so that both uniform corrosion and gross susceptibility to stress-corrosion cracking could be investigated. Two basic water chemistries were used: Hanford basaltic ground water and a NaCl - $MgCl_2$ brine.

All tests were performed at 250°C. Several different metals were suspended in 6.6L-Inconel 600 autoclaves with Hanford basaltic ground water and a 1-L Inconel-625 autoclave for NaCl-$MgCl_2$ brine. For groundwater corrosion tests, the solution was pumped through the crushed basalt at the bottom of the autoclave, as shown in Figure 5.6.

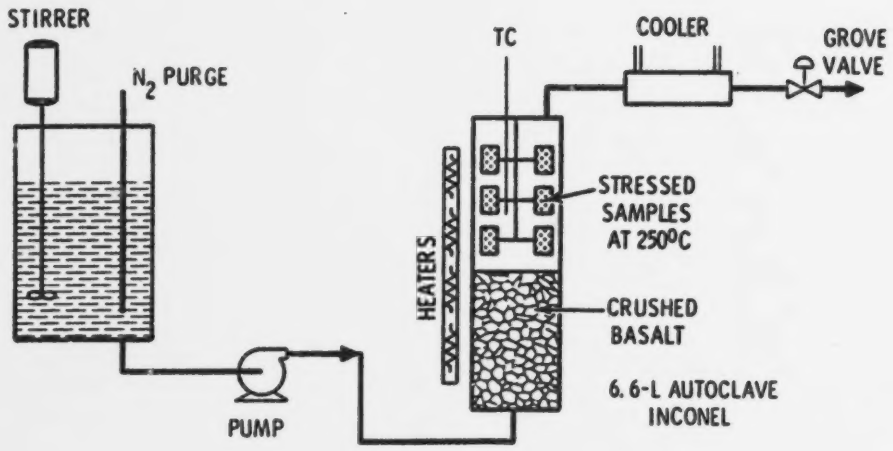

Figure 5.6 Autoclave facility used in Hanford groundwater corrosion tests (Ref. 14).

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Specimens were removed from the autoclaves at suitable time intervals, weighed, cleaned, reweighed, dye-penetrant-checked for cracks, cleaned, re-stressed and returned to the autoclave, or replaced with new samples.

(b) Stress-Corrosion Cracking[15]

The SCC susceptibility of grades 2 and 12 titanium was studied at 250°C in a previously described autoclave system using simulated Hanford groundwater. Wedge-opening load (WOL), (Fig. 5.7), and residual stress specimens, (Fig. 5.8), were used. The latter specimens were plastically deformed in compression, and were allowed to spring back resulting in residual tensile stresses in the material on either side of the hole. No proof of stress-corrosion cracking was obtained from either type of specimen.

5.1.10 BNL HLW Management Research Program

A corrosion research program on HLW container materials has recently begun at Brookhaven National Laboratory, under Nuclear Regulatory Commission sponsorship. The objective of this program is to develop a better understanding of the very slow corrosion mechanisms of high integrity alloys such as Ticode 12 and metals such as titanium, copper and lead. This will help to develop a capability for confirming that container materials selected by DOE can meet the thousand year NRC containment criterion.

Since the current DOE program is focused on screening tests of candidate metals and alloys, BNL is devoting additional effort to the quantitative assessment of the performance of each material, in addition to confirmatory testing. This program includes:

(a) Determination of the existence of critical values for various acceleration variables, outside of which materials remain inert.

(b) Identification of the most probable corrosion mechanisms under repository conditions. Various accelerated test methods, described above are utilized for this purpose. The emphasis will be on thermal, electrochemical radiation and fracture mechanical methods.

(c) Determination of the effects of using more realistic specimen geometries, in addition to previously defined laboratory standard test specimens. One example of this will be the use of a multi-walled container system.

(d) Assessment of the corrosion probability by analytic means, incorporating laboratory test data into the study.

5.1.11 Conclusions and Recommendations

At this time, most work within the DOE corrosion program involves screening assessments of commercial alloys in a repository environment. Only very recently has any fundamental work on corrosion mechanisms begun. No new

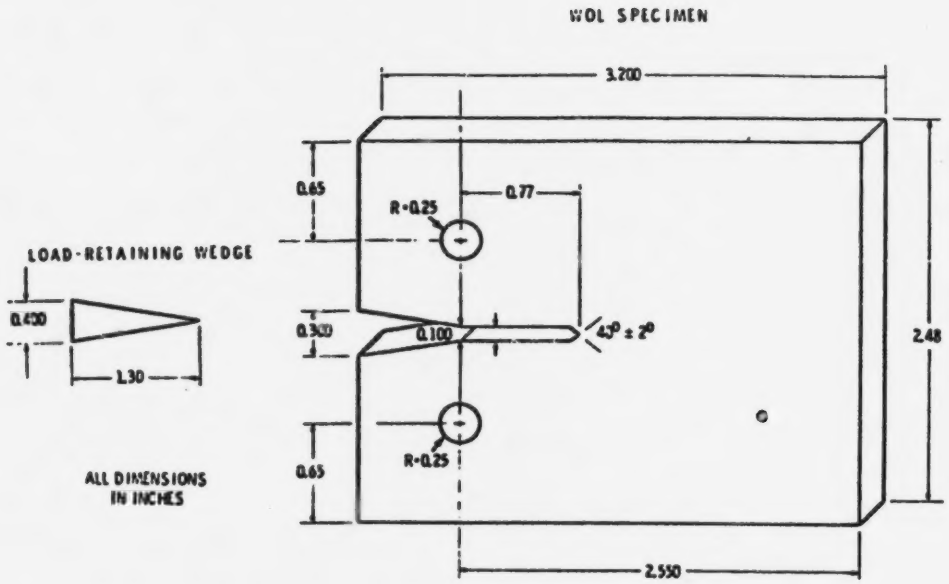

Figure 5.7 Wedge-opening load specimen used for stress-corrosion cracking evaluation in autoclave tests.

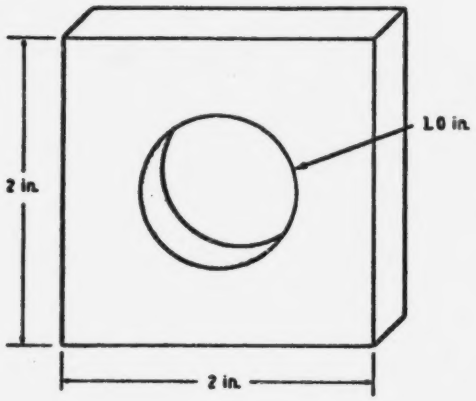

Figure 5.8 Residual stress specimen used in stress-corrosion cracking tests (dimensions in inches).

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tests specific to the long term integrity requirement have yet been generated. Corrosion studies of potential container materials are thus not yet adequate for the requirements contemplated. Clearly, new approaches and technologies are needed to resolve the questions arising from the unprecedented corrosion resistance required for nuclear waste management.

Due to the emphasis on highly corrosion resistant materials, accelerated tests appear inevitable. New accelerated test methods, and new ways to interpret the data from the accelerated tests, should be developed so that the extrapolation of the test results back to non-accelerated conditions and forward to geologic time can be justified.

An MCC workshop on corrosion of engineered barriers has been held, and a ranking of test procedures for each type of corrosion has been derived by consensus. This task group generally agrees with the recommendations from this workshop, including the deliniation of principal areas that will require further consideration beyond current engineering practices; these involve the analyses of pitting, crevice corrosion, and stress corrosion, especially with respect to quantitative predictions of the lifetime of barriers.

The MCC must strongly accelerate the development of specific test procedures to allow their utilization during engineering studies of container designs. For example, according to the present MCC plans, a hydrogen embrittlement delayed failure test is unlikely to be available for some time; we believe that a hydrogen effect study for pure titanium and TiCode-12 is the most important task because they are strongly susceptible to hydrogen embrittlement in certain environments.

Based on the review of recent DOE efforts on corrosion testing, some more specific recommendations are:

1. Test temperature: All DOE contractors have conducted experiments including screening tests at 250°C. As a result, TiCode-12 is the only candidate metal that has not been disqualified so far. Even TiCode-12 has to survive the hydrogen embrittlement test to be a final candidate. This task group believes that the maximum surface temperature of the container should be decreased to near 100°C. With a lower testing temperature, a greater range of metals with different characteristics should be qualified as having suitable lifetime expectancies.

2. Screening tests: This task group feels that uniform corrosion tests can be used as screening tests most effectively. In principle, gravimetric methods (weight change measurements) should give good quantitative results. However, very often it is not easy to separate all corrosion products from the specimen surface; resulting in inaccurate data. Thus, the gravimetric test is not considered sufficiently accurate for screening and it must be supplimented by electrochemical methods, such as the polarization resistance technique. When polarization resistance measurements cannot be used, film thickness should be determined.

Both Sandia and PNL have generated one time-based data point from their screening tests. This task group feels that at least two data points should be generated to illuminate any change in corrosion mechanism with time.

3. Pitting and crevice corrosion: A completely satisfactory test for pitting corrosion does not yet exist. However, electrochemical techniques can be used successfully. Recently, in situ studies on pitting corrosion utilizing the scanning reference electrode technique have been conducted with promising results.[16] We believe that these new approaches should give valid information on localized corrosion as well as pitting corrosion.

4. Stress corrosion: This group recommends CERT and C-ring/U-bend tests as screening tests. We agree with MCC that these tests should be conducted in an aggressive environment, with a high state of stress, and/or with critical strain rates. We also recommend the determination of threshold stress intensities for serious candidate materials.

5. Hydrogen effects: As indicated above since Ticode 12 is the only candidate container metal recommended by a DOE contractor, a hydrogen effect study on this metal is the most important task at this time. This group believes that the slow strain rate test with compact tension specimens is most appropriate for the hydrogen effect study of Ticode 12.

6. The corrosion of welded material must be studied, together with the base materials. Weld structures are often very different from base metal and, as such, could be more susceptible to failure. Evaluation of corrosion (including SCC and pitting corrosion) of welds at the heat affected zones (HAZ) of prospective candidate metals should be carried out.

7. The use of backfill will markedly alter the chemistry of the groundwater and thus will have to be incorporated into test at an early stage.

5.2 Mechanical Testing

5.2.1 Type of Container Test

Mechanical damage to the container is another important area to characterize. While generic testing methods are well developed and standardized in the annual book of ASTM Standards,[17] little effort has been devoted to the evaluation of its mechanical properties. Recently, however, workers at PNL have reported a preliminary study.[13] A brief summary of generic methods potentially applicable to waste management is presented below.

5.2.2 Tensile, Compression, Shear and Torsion Tests

In tensile tests, both the length and the cross section of the sample are measured. With the simultaneous monitoring of applied force, a plot of the stress-strain behavior is obtained. From this curve, the 0.2% off-set from the elastic regime gives the yield stress, and the tensile strength is obtained by dividing the maximum load by the cross-section area. The duration of the test gives the strain rate. Sample shapes are of plate type, sheet type, and round rod type. The sample size and testing procedures are standardized by ASTM, depending on the test materials and test conditions. For example, B557-79 specifies the standard procedure for aluminum, while E21-70[20] is for elevated temperature, and E151-64[21] is for rapid straining. PNL is using round specimens following these standards.[13]

A similar approach is used in compression tests where the compressed length is measured instead of elongation. ASTM E9-77[22] specifies the standard test method. For elevated temperature and high strain rate, the standard methods are given in ASTM E209-65.[23]

The shear test subjects a length of wire, rod or rivet in full cross section to double-shear loading in a tension-testing machine. The shear stress required to fracture the specimen is determined. The standard test specification is given in ASTM B565-76.[24]

The torsion test is for the measurement of the shear stress on a transverse cross section resulting from a twisting action. ASTM E558-75[25] specifies the standard test.

5.2.3 Impact and Tear Test

The essential features of an impact test are: (a) a suitable specimen; (b) an anvil or support on which the test specimen is placed to receive the blow of the moving mass; (c) a moving mass of known kinetic energy which must be great enough to break the test specimen placed in its path, and (d) a device for measuring the residual energy in the moving mass after the specimen has been broken. Charpy Testing and Izod Testing are specifically designed for metal and are standardized in ASTM E23-72.[26] Similar to the waste form characterization, ASTM E208-69[27] specifies the drop-weight test, which employs simple beam specimens prepared to create a material crack in tensile surfaces. The test is conducted by subjecting each of a series of specimens of a given material to a single impact load by a guided, free-falling weight with an energy of 340 to 1630J, depending on the yield strength of the steel to be tested. In the above several methods, the energy input, whether the specimen breaks or not, and the temperature involved are recorded.

The tear test is a drop-weight test to determine the appearance of propagating fractures. The testing machine is either a pendulum type or a vertical-dropped weight type. ASTM E436-74[28] specifies the standard method.

PNL is using the Charpy and Pendulum tests for evaluation of candidate materials[13].

5.2.4 Fracture Toughness Test

This method determines plane-strain fracture toughness of metallic materials using a bend, compact, or cylinder section of a notched and fatigue-cracked specimen. It also determines the specimen strength ratio. This is a function of the maximum load that the specimen can sustain, its dimension, and the yield strength of the material. The method involves tension or three-point bend testing of notched specimens that have been pre-cracked in fatigue. Load vs. displacement across the notch at the specimen's edge is recorded. The load corresponding to a 2% increment of crack extension is established by a specified deviation from the linear portion of the record. The fracture toughness value is calculated from this load on the basis of elastic stress analysis. The specification of the standard test method is in ASTM E399-78a.[29]

Quite often, the material thickness is not sufficient for plane strain to exist at fracture. In this case, non-standard techniques become necessary. PNL[7] is using a J integral test for elastic-plastic fracture toughness. A series of specimens with varying amounts of crack extension are heat treated to mark clearly the area of crack extension; then they are broken. The areas of fatigue pre-cracking and crack extension can be distinguished by the color and texture of the fracture surfaces. The amount of crack extension is measured across the crack front and J is calculated from the extension. The onset of material separation is considered to be the critical value (J_{IC}). Further development of this technique is under way.

5.2.5 Creep and Creep-Rupture Test

This test covers the time-dependent amount of deformation (creep) and the measurement of the time for fracture to occur for materials under constant tension loads at constant temperature. Rupture tests provide a measure of the ultimate load-carrying ability of a material as a function of time, while creep tests measure the load-carrying ability for limited deformations. The two tests supplement each other in defining the load-carrying ability of the material. Precise measurements of the cross-sectional area and original length, and the temperature control are required. The standard method is well described in ASTM E139-70.[30] Currently, MCC is evaluating these tests for container materials and backfill.[31] These tests are usually employed for higher temperature ranges where creep becomes important.

5.2.6 Fatigue Test

The fatigue test is used to determine the effect of variations in material, geometry, surface condition, stress, etc. on the fatigue resistance of materials subjected to direct stress for cycles of varying frequency. The

test is used as a guide to the selection of materials for service conditions of repeated direct stress. Fatigue failure stress or the number of fatigue failure cycles are measured. Depending on the cycles considered, several standard test methods are specified in ASTM E466-76[32] and ASTM E647-78T.[33] Currently, the fatique mechanism study is adopting the fracture mechanics method described in Section 4.3. The standard method has not yet been established. MCC is evaluating these fatigue test methods for use in the canister and overpack materials test.

PNL[13] is adopting center-cracked tension for sheet material and compact tension for plate material. These techniques are standardized and allow fatigue-crack-growth rates to be measured. Various environmental controls also have been used, including a siphon system and a screw-clamp flow control method for solution circulation.

5.2.7 Non-Destructive Evaluation

For quality assurance, it is necessary to evaluate nondestructively the mechanical damage that may occur to the container, as well as the performance assessment in repository conditions. However, little attention is being paid to this area. Some generic testing methods relevant to the package component evaluation are briefly described, as follows:

(a) Leak Test: This method consists of creating a pressure differential across a leak. Therefore, the leak rate is often expressed as the product of some measure of pressure and volume per unit time.

(b) Microwave Inspection: Electromagnetic radiation at the frequency range of 3×10^9 to 3×10^{11} Hz is continuously input or pulsed for the detection of cavities.

(c) Acoustic Emission: Acoustic emission is defined as the high frequency stress waves of strain energy that occur within a material during crack growth, plastic deformation, or phase transformation. The analysis consists of monitoring acoustic emission signals generated by discontinuities in materials under applied stress.

(d) Ultrasonic Inspection: A beam of high-frequency sound waves is introduced into the material for the detection of surface and subsurface flaws. The attenuated and reflected beam is analyzed to define the presence and location of flaws.

(e) Holography: The recorded amplitude and phase of any type of coherent wave motion (either optical or acoustic waves) is called a hologram. At a later time, the wave motion is reconstructed from the hologram by coherent beam in a process that results in the generation of an image having the true shape of the object. This generated image can then be used as a kind of 3-dimensional template against which any deviations in the shape or dimensions of the object can be observed and measured.

(f) Eddy Current Measurement: The principle involved is electromagnetic induction and is used to identify or differentiate between a wide variety of physical, structural, and metallurgical conditions in electrically conductive ferromagnetic and non-ferromagnetic metals. This method is used to determine electrical conductivity, magnetic permeability, hardness, microstructural variation, chemical composition and mechanical damage.

(g) Radiographic Inspection: This method is used for nondestructive inspection of components and assemblies and is based on differential absorption of penetrating radiation -- either electromagnetic radiation of very short wave length or particulate radiation such as alpha radiation --by the part or test piece being inspected.

(h) Thermal Inspection: This comprises inspection by all methods in which heat-sensing devices or substances are used to detect irregular temperatures caused by flaws in the metal.

Some of the above tests are standardized in ASTM[34] and illustrated in part in metal handbooks.[35]

5.2.8 Conclusions and Recommendations

Up to this point very little effort has been devoted to the evaluation of the mechanical properties of container materials. However, the pertinent generic test methods are well-developed and standardized in the annual book of ASTM Standards. These include tests for tensile strength, compression strength, shear and torsion properties, impact and tear strength, fracture toughness, creep and creep-rupture resistance and fatigue resistance.

In order to recommend specific test methods, stress conditions in repository environments should be specified. At present, the lack of such specification makes it difficult to recommend any specific method. For the moment, it is more important to consider what possible mechanical damage could result under repository conditions.

Likewise, many new techniques are available for new nondestructive quality assurance tests. The use of these techniques has apparently not yet been contemplated for whole container tests. It is recommended that any conceptual specification of package design precede the application of these techniques.

For backfill materials, not even generic test methods are available. Standardized generic tests for container materials need to be adopted in the near future for conditions in different backfill media.

5.3 Radiation Effects In Container Testing

5.3.1 Introduction

At the outset, it must be recognized that radiation effects are important only where they affect container durability. The operational measure of container durability is to be provided by tests such as those described above under corrosion testing (section 5.1) and mechanical testing (section 5.2). For metallic containers we do not feel that radiation will introduce any unique failure modes not considered in such tests. From the perspective of container testing, we view radiation as an environmental variable to be included in the generic test procedures, analogous to temperature, media composition, etc.

We begin by describing the radiation environment anticipated for the container and its general effects.

5.3.2 Radiation Environment for the Container

The anticipated radiation environment for a typical radioactive waste container is described in Table 5.2. The following features are illustrated:

- The immediate inner surface of the container may be exposed to fluences of alpha particles, beta particles and heavy ions produced by radioactive delay in the adjacent waste form.
- The bulk of the container, its inner and outer surfaces, and material outside the container may recieve gamma ray doses.

The magnitude of the various particle fluences and gamma-ray doses will depend upon the waste form loading and the internal shielding properties of the entire waste package. Under worst case conditions, heavy ion fluxes will be confined to within a few hundred angstroms of the container's inner surface. Gamma rays are more penetrating but lose their energy by ionization. While some Compton or photoelectrons produced by the gamma rays may have enough energy to displace lattice atoms by elastic collisions, the probability of such events is quite low. For testing purposes, it is important to note that the high gamma flux will occur over the first few hundred years after emplacement; alpha decay effects may not become significant until after the first 1000 years.

5.3.3 Mechanistic Considerations

- It has been recognized for some time that radiation may affect the ability of metals to withstand corrosive attack[38]. This point has received special attention within the nuclear technology community[39,40]. Briefly, there are three ways in which radiation may modify corrosive behavior:

Table 5.2

Radiation Environment for the Container

Radiation	Time Scale	Level at Container Inner Surface	Level at Container Outer Surface	Possible Effects
Alpha-Recoil	10% in 1000 years	$<10^{13}$ atom/cm^2 †	0	o Mild ion implantation o Wasteform volume changes → container stress
Alpha-Particle	10% in 1000 years	$<10^{16}$ α/cm^2 †	0	o mild helium implantation in a thin layer. o Helium pressurization <1000 psi ††
Beta-Particle	~90% in 1000 years	$<10^{18}$ β/cm^2 †	0	o Charge transfer, <1 Coulomb/cm^2 o Displacements in some insulators. Dose ~ 1 ma-hr/cm^2
Gamma Ray	~90% in 1000 years	10^{10} rad	10^{10} rad to $\leq 10^6$ rad	o Ionization/ionization damage o Radiolysis of corrosive media o Effects on passivating Layers

† Our own worst-case estimates, based on data summarized in reference (36). For defense waste, the levels would be at least 10 times lower. For multi-barrier waste forms, the container inner surface would be completely shielded from particle bombardment.

††The amount of helium pressurization will depend on the container design and other variables (37).

(a) by modifying the fundamental bulk properties of the material under test.

(b) by modifying the durability of passivating films or layers.

(c) by changing the nature of the test specimen environment, either through radiolysis of the corrosive media or by degrading waste form or overpack material adjacent to the container.

In general, all three effects may occur simultaneously. Under waste repository conditions, however, we do not expect the bulk properties of metallic containers to be significantly modified, by irradiation. Beta particles and gamma rays are not at all efficient in displacing atoms by elastic collisions. Ionization effects do not produce radiation damage in metals.

- The displacement doses (Table 5.2) anticipated for beta-gamma irradiation are orders of magnitude lower than those (1-10 DPA) commonly required to produce void formation and swelling. Indeed, it is very difficult to find any experimental evidence for gamma ray induced bulk radiation damage in metals.[41]

For certain configurations displacement doses approaching 1 DPA could be produced by recoil nuclei at the very inner surface of the waste form. Under worst case conditions, we view this as a relatively modest ion implantation which will not affect bulk properties. If confirmatory measurements are necessary, the physical and chemical effects of this ion implantation can be simulated and evaluated by standard techniques.

- For composite container systems containing insulating layers, one cannot rule out bulk radiation damage without a specific assessment. We have seen (Chapter 4.4) that insulators can be affected by ionizing radiation; organics are particularly susceptible.

- Hydrogen or corrosive species may be radiolytically produced in adjacent media. Helium will also be produced in the alpha-delay of TRU elements in the waste form. Anticipated radiolysis products for typical waste package designs are shown in Table 5.3. In certain designs, the potential for radiolytic hydrogen embrittlement may exist. The Swedish design cited in Table 5.3 incorporates heavy internal shielding largely to reduce this possiblity. While helium embrittlement is known to occur in certain metals at elevated temperatures[44], this will probably not be significant under repository conditions. The repository will have cooled to ambient temperature before helium production reaches a level where embrittlement becomes a concern (unless the container/waste form design leads to high pressures).

- Irradiation induced stresses may be generated in the container if the waste form expands or contracts during irradiation. Our worst case scoping analysis (section 4.4) indicates that these stresses could be substantial. Helium pressurization may also occur. Finally, for host-rock media such as

Table 5.3

Radiolysis Effects for Different Container Designs

Design	Surface Gamma Dose Rate at Emplacement (rad/hr)	1000 year Surface Gamma Dose (rad)	Radiolysis yields
Reference HLW Container in salt Repository - 10 year old waste	9.3×10^4	2.5×10	H_2: 26 moles/kg H_2O in 20 years
Reference Spent Fuel Container in Salt Repository- 10 year old waste†	1.6×10^4	4.5×10	H_2: 7.4 moles/kg H_2O in 20 years
Swedish Pb/Ti HLW Container in granite repository††		$<10^6$	Equilibrium: $H_2 \leq 8$ g/liter $O_2 \leq 3$ g/liter $H_2O_2 \leq 5.2$ g/liter

† Data from Reference 42. Values given are for brine at the edge of the emplacement hole, and represent maximum specific yields. The radiation dose decreases exponentially with distance from the canister surface. Roughly 12 liters of brine are expected to flow to the HLW container during the first 30 years after burial .

†† Described in Reference 2 and Reference 43. The total dose estimate is our own, from shielding calculations.

rock salt, radiation could change the mechanical properties (i.e. yield point) of material adjacent to the container.[45,46] These factors must be considered when determining the maximum stress to apply in laboratory tests.

5.3.4 Radiation Effects in Corrosion Testing

5.3.4.1 General Testing Methods for Radiation Corrosion

A wide variety of testing methods exists, based largely on the need to evaluate materials performance for nuclear reactor applications. These experiments all employ the same basic technique: The test specimen is contacted with a corrosive environment or medium and both the specimen and medium are exposed to radiation. Following irradiation, specimens, and in some cases the corrosive media, are examined for attack or radiolytic degradation. Experimental configurations vary largely according to the type of radiation employed.

- For heavy charged particle or alpha particle irradiation, the source should be intimately contacted with the test specimen and corrosive medium. Irradiation through windows is generally not practical. Frequently, internal sources are dissolved in aqueous corrosion media.[39]

- Electron bombardment of test specimens and corrosive media can be carried out through thin windows, using external sources. Dose rates up to 10^9 rad/hr can be readily achieved in continuous sources. A number of configurations have been described by Byalubzheski[38]. Electron fluxes are probably the easiest to control of any radiation source; Moreover, electrons of different energies can be used to distinguish between displacement damage and ionization effects. However, the need to irradiate through a thin window limits the ability to conduct experiments at elevated pressure.

- Gamma irradiation of test specimens and leachants can be conducted for a wide variety of experimental geometries. Gamma irradiations can be made at elevated temperatures and pressures in thick walled autoclaves. In general, it is more difficult to regulate gamma dose than electron dose. Gamma dose rates may be controlled either by varying the amount of shielding or by varying the source-to-specimen distance[38].

As mentioned earlier, corrosion is commonly studied by observing the specimen after it has been removed from the radiation field. However, it is often advantageous to monitor or change conditions in the test cell during irradiation. This may be done in a number of ways.

- To monitor or control conditions in the corrosive medium during irradiation "loops" may be constructed in which the medium is circulated through the specimen/irradiation cell.[38] The feed can be changed to control input pH, composition, etc. and the output may be analysed for corrosion or radiolysis products. A typical system has recently been described by Isisigure, et. al.[49].

• Electrode potential measurements may be carried out to monitor the state of surface films during irradiation. The techniques employ a standard electrode and are basically similar to those described in section 5.1. It is worthwhile to point out that, if the radiation produces a net charge displacement ("radiation polarization"[38]) in the electrolyte-specimen system, electrochemical effects may be promoted. This effect is generally associated with charged particle irradiations, and the extent of polarization depends upon dose rate and the conductivity paths present.

5.3.4.2 Development of Radiation/Corrosion Container Tests by DOE

Only a very few tests have been specifically designed to evaluate container corrosion under anticipated waste repository conditions. These tests are of the screening variety and concentrate entirely on evaluating corrosion under gamma irradiation.

• Braithwaite and co-workers[5,47,48] carried out corrosion measurements on metal coupons contacted with salt brines during gamma irradiation at elevated temperatures. The irradiations were carried out in sealed quartz tubes (over half of which were either attacked or exploded during exposure). No mention was made of specific sample configurations to evaluate crevice corrosion, hydrogen embrittlement, etc. Parameters such as internal pressure and solution pH were allowed to vary during the irradiations.

• Currently, workers at PNL[50] are constructing an irradiation/corrosion test fixture for corrosion studies during gamma irradiation (Figure 5.9). The device incorporates an autoclave, with provision for monitoring electrode potentials and corrosive media chemistry during irradiations. This equipment is expected to become operational during the latter part of FY81; It represents an ambitious step toward the development of a second generation of test facilities.

• Recently the Materials Characterization Center has convened a workshop[18] specifically addressing container corrosion testing. We wholeheartedly subscribe to the central theme of the workshop, i.e. that the principal challenge of container corrosion testing is to scale and extrapolate short-term test results to predict 1000-year performance. The workshop specifically identified radiation as an important external variable, on a par with temperature, and singled out several areas for test development. (Table 5.4) At this point no specific test procedures have been advanced; consequently, it is not clear how the MCC proposes to deal with the problem of scaling and extrapolating short-term radiation/corrosion test data to predict repository performance.

5.3.4.3 Discussion of Issues in Test Development

Those tests which are currently under design or being carried out emphasize the effects identified as (b) and (c) in section 5.3.3. As mentioned,

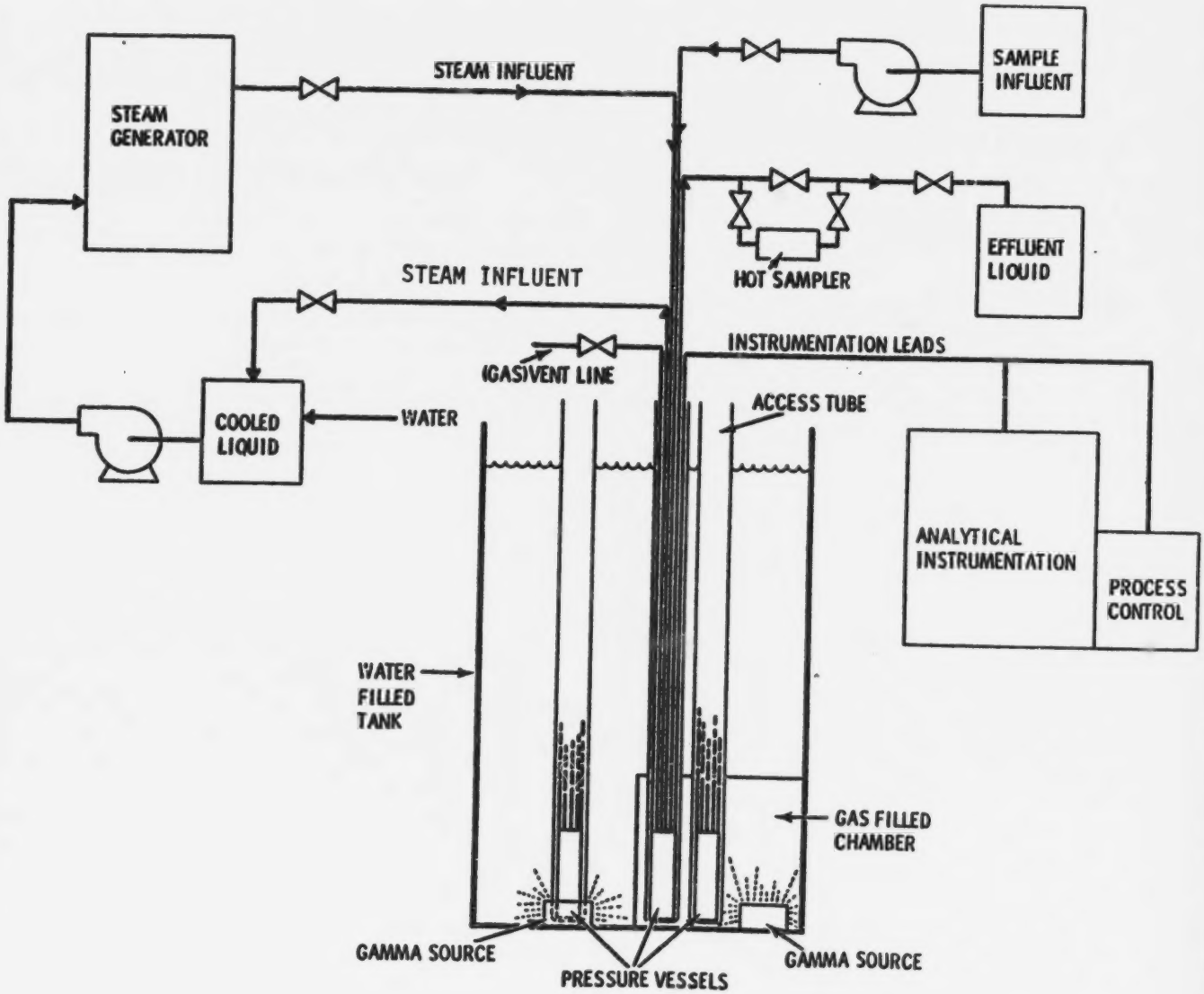

Figure 5.9 Radiation/corrosion test fixture under development at Pacific Northwest Laboratories. We understand the steam heating system is to be replaced by resistance heating[50].

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Table 5.4

MCC Proposed Engineered Barrier Radiation Corrosion Tests[18]

Test #	Title	Description
13 MCC-EB13	Radiation Corrosion Test	Coupon Immersion, Autoclave & Radiation
14 MCC-EB14	Radiation-Crevice Corrosion Test	Contrived Crevice Autoclave & Radiation
15 MCC-EB15	Radiation C-Ring SCCS	Autoclave & Radiation

it is commonly held that the most important corrosion effects in a gamma-radiation environment occur due to the radiolysis of corrosive agents.[38,43-47,48] We shall consider this point first.

- Radiolysis of corrosive media.

To quote Braitwaite and Molecke[49]:

"Effect of Radiation: Several alloy specimens were exposed to 90°C brines in the presence of gamma radiation (10^7 R/hr, integrated dosage 1-2X10^{10}R) from a ^{60}Co source. A number of preliminary conclusions can be drawn:

(1) the principal effect on corrosion is due to the production of radiolysis products;

(2) the quantity of radiolysis products formed increases with increases in the dose rate, the total dose, and the concentration of solids dissolved into the irradiated solution; and

(3) at dose rates typical of high level waste, the corrosion rate of 1018 mild steel is doubled, while that of stainless steel, Inconel 625, and Ticode-12 are just detectably increased. The increases in rate are probably due to a slight increase in the oxidizing potential of the solution..."

It is significant that the quantity of radiolysis products (as well as corrosion rates) is said to depend upon dose rate as well as total dose; apparently the test can be accelerated by increasing the dose rate. Under these conditions, a question arises - should one test at realistic dose rates or

realistic total doses? The answer depends on which method demonstrably provides worst-case conditions. The problem is sensibly identical to that considered earlier (section 4.4) under "Radiolysis of Leachants." Here, a major task is to relate the corrosion rate to the radiation dose rate. Research is required to determine how this should be done.

To illustrate by an elementary example, assume that the radiation corrosion rate, ΔR, is proportional to the concentration of a particular radiolysis product, C_o:

$$\Delta R = k_1 C_o \tag{1}$$

Next assume that the steady state (or adiabatic) concentration of the product is proportional to some power of the radiation dose rate, ϕ

$$C_o = k_2 \phi^{\mu} \tag{2}$$

Combining (1) and (2)

$$\Delta R(t) = k_1 k_2 (\phi(t))^{\mu} \tag{3}$$

Under these conditions it is straightforward to determine the radiation dose rate scaling. Suppose that in a laboratory experiment an irradiation dose is administered which is equivalent to the total gamma dose administered in the repository. Let the laboratory dose be administered over a time t_L. By virtue of (3) the total corrosion expected in the repository (R_R) is related to that measured in the laboratory (R_L) by

$$R_R = R_L \frac{1}{\mu} (\tau/t_L)^{1-\mu} \tag{4}$$

In (4), τ is the decay constant for the radionuclide producing the repository gamma dose. For ^{137}Cs and ^{90}Sr, $\tau \simeq 45$ years.

A commonly cited value for μ in Equation (2) is 1/2 [50]. Burns and Moore[40] have carried out a calculation of radiolysis yields in a study of Zircaloy corrosion in reactors. Their results lead to a value for μ of approximately 5/8. In Braithwaite and Molecke's experiment, at a total dose of 10^{10} rad, $t \simeq 40$ days. Taking $\mu = 1/2$ and assuming that (4) holds one would expect about forty times more corrosion in the repository than that observed in the Sandia Lab experiments.

We do not offer the above analysis as anything more than an illustrative example. There is some experimental evidence in support of Equation (2)[51]; no general claims can be made as to the validity of Equation (1).[38]. Only limited experimental data are available comparing radiation corrosion at different dose rates. There are apparently some cases in which increased net corrosion is observed at lower dose rates.[38] Consequently, we consider the effect of radiation dose rate on corrosion rates as the major issue which remains to be addressed in extending the present screening radiolysis/corrosion tests to predict long term behavior.

- Radiation Effects on Passivating Layers.

Here we are concerned with the direct effects of gamma radiation on surface films themselves, rather than those solution radiolysis effects which may indirectly affect film buildup. There are two sorts of direct effects to consider; First, radiation damage, including ionization effects and charge buildup could presumably occur in insoluble insulating layers (e.g., corrosion films) on or near metal surfaces. Second, the conductivity of highly insulating oxide layers such as TiO_2 can be increased during ionizing radiation, which might affect electrochemical corrosion processes.[32,52]

While the significance of these effects under gamma irradiation is doubtful in comparison to effects on solution radiolysis, some assessment is warranted in view of the stringent requirements on containers and the localized nature of corrosive attack. The behavior of passivating layers can be monitored by observing changes in the electrode potentials when the irradiation dose rate is changed or by corrosion measurements on surfaces illuminated with UV radiation.[38] A major virtue of testing during irradiation, however, is that both radiolysis effects and changes in the passivating layer are observed simultaneously, i.e. the net effect of radiation is displayed.

It is probably not necessary to test separately for, or differentiate between, radiolysis effects and radiation induced-changes in the passivating layer, provided that it can be demonstrated that these effects retain their relative importance in laborat and repository conditions.

- Radiation Corrosion at the Container-Waste Form Interface

We are not aware of any tests which have specifically been developed to evaluate radiation effects on container-waste form interactions.(Table 5.2) While critical evaluation may fall in the category of whole package testing, some useful screening tests could and should be carried out during the container test program. Screening evaluations should be carried out for various waste-form container configurations to identify those cases (if any) where further detailed testing may be necessary. This could be done, for example, by subjecting waste form-container sandwiches to electron irradiation at elevated temperatures, by contacting waste form material with ion-implanted container material, or in some cases by calculation.

- Radiation Corrosion during Storage/Handling

Here we simply point out that container radiation corrosion could occur at any point prior to geologic emplacement, if the proper conditions exist. Russian workers,for example, have observed "radiochemical effects" at the surfaces of waste forms and containers stored in air[53]. As mentioned earlier, nitric acid is produced in the radiolysis of air-water systems[54]. Although such effects may not be large in comparison with those anticipated in the repository, corrosion during storage might precipitate or accelerate long-term attack. Consequently, some effort should be expended to ensure that containers will not be degraded (or sensitized) by radiation corrosion during storage or handling. Here one might draw on spent fuel pool experience.

5.3.5 Radiation Effects in Mechanical Testing

5.3.5.1 General Testing Methods for Irradiation Effects on Mechanical Properties

Standard testing methods for radiation effects on mechanical properties are specified in ASTM E184-62. The test emphasizes those changes (increased hardness, yield strength, tensile strength and notch-impact transition temperature; decreased ductility and fracture energy; changes in deformation and fracture characteristics) which occur under neutron or energetic particle bombardment. The specimen is irradiated and subsequently tested as described in section 5.2. Standard methods for testing during irradiation have not yet been specified.

5.3.5.2 Development of Radiation/Mechanical Property Container Tests by DOE

Very few tests have been carried out or designed to specifically evaluate radiation effects on container mechanical properties under anticipated repository conditions. Early observations on container durability under gamma irradiation were made in Project Salt Vault[55]. Again, the Sandia group appears to be pioneering recent efforts. They have reported results obtained in their radiation corrosion measurements which at least suggest the embrittlement of Ticode-12 by radiolytic hydrogen.[46,47]

Container materials, contacted with waste form and overpack materials, are being irradiated in the WRIT program whole package tests. We understand that a part of this effort, the mechanical properties of the container material are to be examined, subsequent to the hot cell test. These measurements are currently underway in FY81.

5.3.5.3 Discussion of Issues in Test Development

At this point, little effort has been directed toward developing specific tests to evaluate radiation effects on mechanical properties of HLW containers. This lack of emphasis, may reflect two conceptions:

(a) The bulk properties of metallic containers will not be affected by irradiation under repository conditions.

(b) Radiation associated effects such as hydrogen embrittlement will be either displayed in radiation-corrosion or whole package hot-cell tests, or can be tested for in simulations without irradiation.

• We subscribe to the first of these viewpoints and do not recommend extensive testing for bulk degradation of pure metallic containers. We do feel however, that careful confirmatory considerations should be undertaken to demonstrate the anticipated bulk mechanical durability of realistically fabricated container materials at repository doses. There is at present no

prescription for testing radiation effects on the "bulk" properties of multi-layer containers. The importance of such tests will depend upon the materials chosen. Generally we feel that metal-insulator systems designed to withstand thermal stresses developed by decay heating should probably be fairly durable against differential radiation-induced expansion in insulating layers. Before a test procedure can be specified in detail, the radiation damage susceptibility of the insulating barrier must be investigated. A number of refractory oxide materials should prove reasonably durable; organics or concretes would require critical testing.

- If the concentrations of hydrogen, helium or other radiolytic gases produced under repository conditions can be confidently estimated, screening gas phase embrittlement tests can be carried out without irradiation.† However, as for radiation corrosion, it may be in some cases difficult to relate these results to repository performance with any precision. One must then determine for example, whether the presence of radiation and/or corrosion markedly affects the mechanism of gas uptake. There is apparently little evidence either way on this, although we do not generally expect major radiation - related effects. In critical cases then, we feel that gas-phase embrittlement experiments should be carried out in an irradiation field under conditions which are as realistic as possible. There is probably no reason why corrosion measurements could not be carried out simultaneously. The central emphasis should be to determine if radiation and/or radiation corrosion will affect the uptake mechanism. This philospophy may be incorporated de facto in the whole package hot cell tests planned in the WRIT program.

5.3.6 Testing and Testing Research Recommendations

In this section we identify the types of tests which will be required to satisfactorily evaluate container durability in light of draft NRC performance objectives. Where possible, specific procedures are recommended. Where no recommendation is possible at this point, research requisite to the development of acceptable test procedures is specified.

5.3.6.1 Recommendations for Radiation Corrosion Testing and Research

In general, we anticipate that specific tests will be needed to evaluate or confirm the effect of radiation on the various corrosion mechanisms described in section 5.1. These tests fall into two classes.

(a) Scoping or comparative tests which may be useful in selection of candidate designs and determining design sensitivity.

(b) Confirmatory or critical tests necessary for licensing evaluations. These must provide the information required to assess long term performance under repository conditions.

†In the Swedish container designs, "tests" of this sort have been carried out entirely by analytic methods.

Thus far, only tests in category (a) have been developed and applied to container materials, and these at a fairly rudimentory level. Development of second generation tests addressing specific mechanisms is either anticipated or currently under way, as indicated in section 5.3.4. However, it is not yet possible to identify any specific test procedure in category (b) which we presently consider acceptable for licensing.

- The major outstanding question which must be addressed before a radiation/corrosion test can be qualified for licensing is the dependance of test results on radiation dose rate. In particular, it is essential to understand how the corrosion rate, or time to failure, depends upon radiation dose rate. We recommend that confirmatory or critical radiation/corrosion tests should achieve radiation doses commensurate with those anticipated in the repository. For gamma irradiation, we expect that this will require a laboratory dose rate which is at least 30 times greater than that anticipated in the repository. Research should continue to determine how to (conservatively) relate corrosion data at laboratory dose rates to anticipated results at repository dose rates. The obvious way to proceed is to carry out otherwise identical laboratory tests during irradiation at different dose rates. These tests can be done simultaneously under gamma irradiation (in fact, in the same vessel[38]) without excessive difficulty.

- We expect that, under repository conditions, the dominant mechanism in radiation corrosion will involve formation of gamma radiolysis products. The identity and concentration of radiolysis products anticipated in various repository environments should be specified as promptly and accurately as possible. These estimates should be made as a function of gamma radiation dose and dose rate. These anticipated radiolysis products could then be incorporated into the tests defined in section 5.1 to provide a first-order simulation of radiation effects to aid in test development.

- Other possible corrosion mechanisms could involve radiation induced conductivity in passivating layers, radiation polarization (charge transfer) or radiation enhanced diffusion in environmental media. We recommend that the relative importance of these various mechanisms be established. A useful consideration in such studies would be whether or not the major corrosion mechanism depends on the formation of a long lived species. Effects such as conductivity changes, radiation polarization or enhanced diffusion might be termed "radiation dynamic" i.e. involving electronic mechanisms which effectively cease to operate once the radiation is turned off. On the other hand, radiolysis could include both a radiation dynamic component (formation of short-lived radicals, etc.) and a long-lived "static" component involving generation of "stable" species such as H_2, H_2O_2, HNO_3, etc. An extremely useful way to distinguish between static and dynamic effects is to monitor the system while the radiation dose rate is charged.[38,54]

- Static effects (long-lived radiolysis products, etc.) once they are understood, might be fairly well simulated in tests without irradiation. We recommend, however, that all critical or confirmatory radiation testing be carried out during irradiation up to doses anticipated in the repository, in realistic groundwaters at realistic temperatures. The container material should also be contacted with waste form and overpack media. Solution chemis-

try and/or electrode potentials should be monitored during the test. At a minimum, such tests will be required to confirm the validity or conservativeness of simulations without irradiation. If radiation-dynamic effects are significant, testing during irradiation becomes the only alternative. The test fixture under development at PNL (Figure 5.9) appears to have the capability to perform critical or confirmatory tests of this nature.

5.3.6.2 Recommendations for Radiation/Mechanical Property Testing

We do not feel that extensive testing for gamma radiation effects on bulk metal container properties will be required. Confirmatory measurements could be carried out in conjunction with corrosion testing. The areas where further consideration may be warranted include: (a) effects of gamma irradiation on metal-insulator composite systems, (b) embrittlement at interior or exterior surfaces by helium or radiolytically produced gases and (c) possible stresses transmitted to the container by radiation-induced volume changes in the waste form. This possibility should also be considered in evaluating stress corrosion.

- None of these areas appears to represent a major challenge in test development. Techniques have been discussed in sections 5.1 and 5.2 for scoping measurements. Again, insofar as radiation effects are concerned, the principal tasks are to: (a) establish the anticipated radiation effects on the environment (gas generation waste, form swelling, etc.), (b) determine if the particular failure mode under study involves "radiation-dynamic" effects which cannot be conservatively simulated without extensive testing during irradiation; (c) determine how to conservatively relate results at laboratory dose rates to repository conditions.

- Effects such as waste form swelling, helium build up and displacement damage at inner container walls may be entirely negligible if the container is required to last for 1000 years or less. On the other hand, we anticipate a need for a standard radiation/hydrogen embrittlement test. Scoping measurements can be carried out without irradiation. Research, however may be necessary to determine if the mechanism of hydrogen uptake will be influenced by the presence of a radiation field.

5.4 References

1. T. E. Scott, "Issues Relevant to Nuclear Waste Canister Materials," paper No. 210, presented at NACE Corrosion/80, Chicago, Il. (March 3-7, 1980).

2. KBS (Sweden) Technical Report #107, "Lead-lined Titanium Canisters for Reprocessed and Vitrified Nuclear Fuel Waste - Evaluation of Corrosion Aspects," (1978).

3. J. W. Braithwaite, N. J. Magnani and J. W. Munford, "Titanium Alloy Corrosion in Nuclear Waste Environments," Sandia National Laboratory Report #SAND79-2023 (1979).

4. M. G. Fontana and N. D. Greene, Corrosion Engineering, 2nd ed. McGraw-Hill Book Co., 1978. p. 28.

5. J. W. Braithwaite and M. A. Molecke, "Nuclear Waste Canister Corrosion Studies Pertinent to Geologic Isolation," Nuclear and Chemical Waste, 1, 37 (1980).

6. H. H. Uhlig, Corrosion and Corrosion Control, John Wiley and Sons, N.Y. 1971.

7. F. L. Laque, Marine Corrosion Causes and Prevention, John Wiley and Sons, N. Y. 1975.

8. D. W. Shannon, "The Role of Chemical Components in Geothermal Brines on Corrosion," Paper 57, Presented at Corrosion 78, NACE, Houston, TX. (1978).

9. G. H. Jenks, "Radiolysis and Hydrolysis in Salt-Mine-Brines," ORNL-TM-3717, Oak Ridge National Laboratory Report, (March 1972).

10. M. D. Merz, G. E. Zima, R. H. Jones and R. E. Westerman, "MCC Workshop on Corrosion of Engineered Barriers - Summary Report," Pacific Northwest Laboratory Report (March 1981).

11. M. D. Merz, G. E. Zima, R. H. Jones and R. E. Westerman, "MCC Workshop on Corrosion of Engineered Barriers - Summary Report," Pacific Northwest Laboratory Report p. 18, (March 1981).

12. M. A. Molecke and L. Abrego, "Status of Sandia HLW Canister/Overpack Program Studies," Sandia National Laboratory Report , SAND80-2191C, UC-70., (December, 1980).

13. R. E. Westerman, "Investigation of Metallic, Ceramic, and Polymeric Materials for Engineered Barrier Applications in Nuclear-Waste Packages," Pacific Northwest Laboratories Report, PNL-3484, UC-70, p. 14., (October 1980).

14. "Metallic Materials Corrosion Properties Evaluation," ibid. p. 47.

15. "Metallic Materials Mechanical Properties Evaluation," ibid. p. 29.

16. H. S. Isaacs and B. Vyas, ASTM Symposium on Progress in Electrochemical Corrosion Testing, San Francisco, May 1979.

17. Annual Book of ASTM Standards, Part 10, Metals-Physical, Mechanical, Corrosion Testing, American Society for Testing and Materials (1980).

18. ASTM E8-79, "Standard Method of Tension Testing of Metallic Materials".

19. ASTM B557-79, "Standard Testing of Wrought and Cast Aluminum and Magnesium Alloy Products".

20. ASTM E21-70, "Standard Recommendation Practice for Elevated Temperature Tension Tests of Metallic Materials.".

21. ASTM E151-64, "Standard Recommendation Practice for Tension Tests of Metallic Materials at Elevated Temperatures with Rapid Heating and Conventional or Rapid Strain Rates".

22. ASTM E9-77, "Standard Methods of Compression Testing of Metallic Materials at Room Temperature".

23. ASTM E209-65, "Standard Recommended Practice for Compression Tests of Metallic Materials at Elevated Temperatures with Conventional or Rapid Heating Rates and Strain Rates".

24. ASTM B565-76, "Standard Method for Shear Testing of Aluminum and Aluminum-Alloy Rivets and Cold-Loading Wire and Rods".

25. ASTM E558-75, "Standard Method for Torsion Testing of Wire".

26. ASTM E23-72, "Standard Bar Impact Testing of Metallic Materials".

27. ASTM E208-69, "Standard Method for Conducting Drop-Weight Test to Determine Nil-Ductility Transition Temperature of Ferritic Steels".

28. ASTM E436-74, "Standard Method for Drop-Weight Tear Tests of Ferritic Steels".

29. ASTM E399-78a, "Standard Test Method for Plane Strain Fracture Toughness of Metallic Materials".

30. ASTM E139-70, "Standard Recommended Practice for Conducting Creep, Creep-Rupture, and Stress-Rupture Tests for Metallic Materials".

31. "Composite Quarterly Technical Report on Long-Term HLW Technology," October-December 1979, Savannah River Laboratory Report DP-79-157-4 (1980).

32. ASTM E466-76, "Standard Recommended Practice for Constant Amplitude Axial Fatigue Tests of Metallic Materials".

33. ASTM E647-78T, "Tentative Test Method for Constant-Load-Amplitude Fatigue Crack Growth Rates Above 10^{-8}m/Cycle".

34. Metal Handbook, 8th Ed., Vol. II, Nondestructive Inspection and Quality Control (1976).

35. Annual Book of ASTM Standards, Part II, Nondestructive Testing, American Society for Testing and Materials (1980).

36. F. P. Roberts, R. P. Turcotte, W. J. Weber, "Materials Characterization Center Workshop on The Irradiation Effects in Nuclear Waste Forms -Summary Report," Pacific Northwest Laboratory Report, PNL 3588/UC-70 (January, 1981).

37. R. P. Turcotte, "Radiation Effects in Solidified High Level Waste, Part 2, Helium Behavior," Pacific Northwest Laboratory Report, BNWL-2051 (May 1976).[1]

38. A. V. Byalobzheskii, Radiation Corrosion, (U. S. Atomic Energy Translation AEC-Tr 7096 (1970). [2]

39. G. H. Jenks, Oak Ridge National Laboratory, "Review and Correlation of In-Pile Zircalloy-2 Corrosion Data and a Model for the Effects of Radiation," Oak Ridge National Laboratory Report, ORNL 3039, (1963).

40. W. G. Burnes and P. B. Moore, "Water Radiolysis and its Effect Upon In-Reactor Zircally Corrosion," Radiation Effects, 30: 233 (1976).

41. N. Q. Lam and S. J. Rothman, "Radiation Enhanced Diffusion in Metals and Alloys," in Radiation Damage in Metals, H. L. Peterson and S. D. Harkness, Eds., (American Society for Metals, Metals Park, Ohio, 1976), pp. 125-156.

42. G. H. Jenks, "Review of Information on the Radiation Chemistry of Materials Around Waste Canisters in Salt and Assessment of the Need for Additional Experimentation," Oak Ridge National Laboratory Report, ORNL-5607, March, (1980).

43. P. E. Ahlstrom, "Ceramic and Pure-Metal Canisters in Buffer Material," p. 285, in High-Level Solid Radioactive Waste Forms, USNRC Conference Proceedings, NUREG/CP-0005, December 1978.

44. E. E. Bloom, "Irradiation Strengthening and Embrittlement," p. 295, in Radiation Damage in Metals, N. L. Peterson and S. D. Harkness, Eds., (American Society for Metals, Metals Park, Ohio, 1976).

45. B. D. Gunter and F. L. Parker, Oak Ridge National Laboratory, "The Physical Properties of Rock Salt as Influenced by Gamma Rays," Oak Ridge National Laboratory, ORNL-3027, March, (1961).

46. F. Aguillo-Lopez and P. W. Levy, "Effects of Gamma-Ray Irradiation on the Mechanical Properties of NaCl Single Crystals," Proc. Brit. Ceram. Soc. 1, 183, (1964).

47. J. W. Braithwaite, N. J. Magnani, and J. W. Munford, "Titanium Alloy Corrosion in Nuclear Waste Environments," in Corrosion/80, NACE, Paper #213, Proc. of Conference held March 1980, Chicago.

48. J. W. Braithwaite and N. J. Magnani, "Corrosion Considerations for Nuclear Waste Isolation Canisters," in Scientific Basis for Radioactive Waste Management, V.1, G. J. McCarthy, Ed., (Plenum Press, NY, 1979) p. 283.

49. K. Isisigure, et. al. "Effect of Gamma Radiation on the Release of Corrosion Products from Carbon Steel and Stainless Steel in High Temperature Water," Nucl. Tech. 49, (1980).

50. S. Pitman and R. Elmore, Pacific Northwest Laboratories, Private Communication.

51. E .V. Egorov and P. D. Novikov, Action of Ionizing Radiation of Ion Exchange Materials, (Israel Program for Scientific Translations, Jerusalem, 1967) p. 80.

52. R. W. Klaffky, B. H. Rose, A. M. Goland, and G. J. Dienes, "Radiation-Induced Conductivity of Al_2O_3: Theory and Experiment." To appear in Phys. Rev. B. Available in preprint form as Brookhaven National Laboratory Report BNL-26499. (1981)

53. A. S. Nikiforov, et. al., "Thermal, Chemical and Radiation Stability of Vitreous Radioactive Wastes," in Scientific Basis for Radioactive Waste Management, V. I, G. J. McCarthy, Ed., Plemun Press, NY, 1979), pp. 117-121.

54. A. R. Jones, "Radiation Effects on Water," Radiation Research, 10: 655, (1959).

55. R. L. Bradshaw and W. C. McClain, Editors, "Project Salt Vault: A Demonstration of the Disposal of High-Activity Solidifed Wastes in Underground Salt Mines." Oak Ridge National Laboratory Report, ORNL-4555, UC-70 (April 1971).

6. BACKFILL TESTING FOR RADIONUCLIDE MIGRATION

6.1 Introduction

The purpose of backfill in nuclear waste isolation is to serve as a redundant barrier and augment the radionuclide isolation and retardation capabilities of the nuclear waste package. The backfill fulfills this function by interacting chemically with the released radionuclides and/or by presenting them with a nearly impermeable barrier, thereby retarding their migration from the waste package. The primary concern in testing backfill materials is to provide the information required to evaluate the radionuclide retardation capabilities (i.e., breakthrough times and sorption capacities) of candidate backfills in a quantitative manner and do so under conditions most representative of the repository environment.

A valid testing program must seek to reproduce the hydrologic, thermal, chemical and radiologic environment in which backfills will be required to perform. These goals can be achieved in the laboratory by testing backfills utilizing dynamic flow-through column testing methods and mass-balance modeling techniques similar to those applied by chemists, geochemists and hydrologists to porous beds, sediments and soil.[1-10]

It should be pointed out that while this section considers tests which deal with the radionuclide retardation capabilities of backfills, so as to be able to address regulatory criteria, it is assumed that the candidate materials will possess other attributes which are necessary so that they can function properly in the repository environment. The backfills must have adequate mechanical properties such as bearing capacity, swelling pressure and plasticity to accommodate host rock shifting due to stresses and settling and maintain a homogenous barrier. The backfill must be stable in the thermal, chemical, and radiation environments present in the repository. The backfill must also be compatible with the waste container and with the host rock over geologic time scales. Mechanical and synergistic effects on backfill sorption capacity are not considered in this present report.

In this chapter, the processes controlling radionuclide migration through a backfill are first considered. Then a column testing procedure is proposed for the derivation of retardation factors and diffusion coefficient, leading to their use in a mathematical flow model. The effect of radiation on the testing process is also considered.

6.2 Background - Processes Controlling Radionuclide Migration

In order to successfully test backfill materials for their radionuclide retention properties, one must be aware of the principal processes which control radionuclide migration in porous media. Such processes can be divided into transport processes and retardation processes. As described by Ahn, Dayal, and Wilke,[11] the primary radionuclide transport processes include advection, dispersion and molecular diffusion. The processes which retard radionuclide migration consist of a group of reactions which occur between dissolved radionuclides and the backfill material which are collectively known as sorption processes.

6.2.1. Transport Processes

Transport by advection simply means transport via the bulk pore water flow through the backfill. Advection is proportional to the groundwater velocity and the advective flux can be expressed as

$$F_a = UC \qquad (6.1)$$

where F_a = advective flux $(\frac{M}{L^2 \cdot t})$

U = groundwater velocity $(\frac{L}{t})$

C = solute concentration $(\frac{M}{L^3})$

An idealized concentration profile as generated by advection processes is given in Figure 6.1.

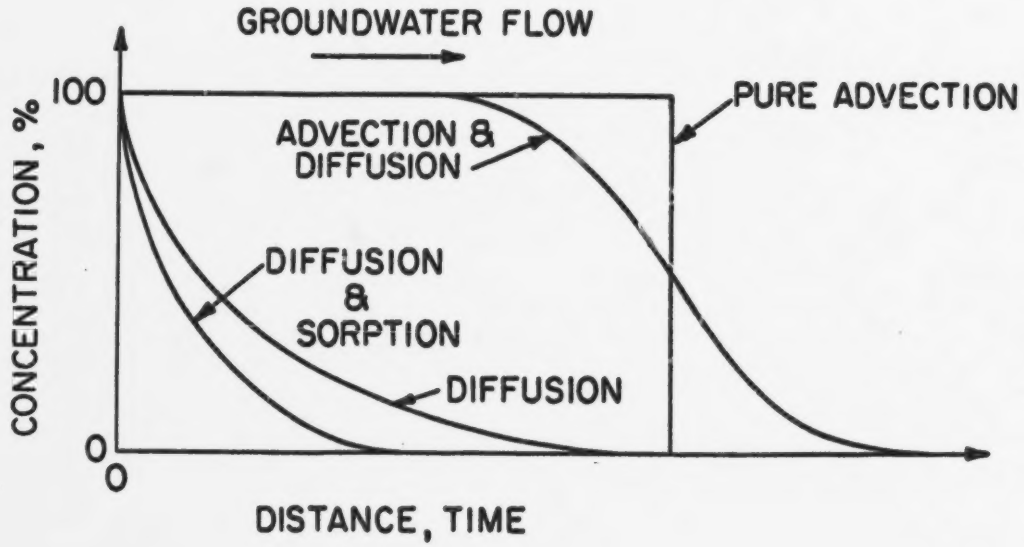

Figure 6.1. Idealized depiction of radionuclide transport processes through backfill given a continuous source. Diffusion as used with advection includes effects of dispersion.(30)

Dependent upon the conditions in the backfill bed, pure advection can be modified by the process of dispersion. Dispersion is caused by velocity gradients in porous media produced by friction between the flowing groundwater and the surface of the particles in the bed. These velocity gradients spread out the advective front and skew the concentration profile relative to that produced by advection. This can act to shorten radionuclide breakthrough

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times as depicted in Figure 6.1. Dispersion is a function of the groundwater velocity and the bed particle size. As we will see later, dispersion is of secondary importance and, depending upon the circumstances, can be assumed insignificant.

A third process of importance to radionuclide transport is that of molecular diffusion. Due to probabilistic considerations, diffusion results in the transport of solute molecules or ions from regions of high concentration to regions of low concentration. The diffusive flux can be mathematically expressed as

$$F_D = - D \left(\frac{dC}{dx}\right) \tag{6.2}$$

where F_D = diffusive flux $\frac{M}{L^2 \cdot t}$

D = coefficient of diffusion $\frac{L^2}{t}$

$\frac{dC}{dx}$ = concentration gradient $\left(\frac{M}{L^4}\right)$

also known as Fick's First Law of Diffusion. The net effect of molecular diffusion is similar to that of dispersion in that it can affect advective transport, causing a skewed concentration profile relative to that produced by advection alone and thereby hasten breakthrough (Figure 6.1). Diffusion alone, however, is a very slow transport process relative to what can occur due to advection. Molecular diffusion is a direct function of the concentration gradient and is independent of groundwater flow rate. Because of this, molecular diffusion can contribute to radionuclide transport over the entire range of flow rates expected in repositories, though it may not always be significant. At this point, a few words about the nature of the diffusion coefficient would be useful to help prevent confusion later on. There are different kinds of diffusion coefficients and it is important to understand what they represent and when they are valid.

The most fundamental diffusion coefficient is known as the simple diffusion coefficient and this deals strictly with the diffusion of ions in bulk solution. In porous media like backfill, however, the situation becomes more complex. In cases where there is no interaction between an ion and the porous media, diffusion is slowed due to the tortuous path an ion or molecule must follow. The diffusion coefficient which takes this effect into account is known as the whole sediment diffusion coefficient[13,37-39] and is expressed as

$$D_S = \frac{D}{\Theta^2} \tag{6.3}$$

where D_S = whole sediment diffusion coefficient $\left(\frac{L^2}{t}\right)$

D = simple diffusion coefficient $\left(\frac{L^2}{t}\right)$

Θ = tortuosity of porous media

The tortuosity of a porous media is defined as the ratio of the actual path length to the straight-line distance. In situations where the diffusing ions interact with the bed material, such as ion-exchange, the diffusion coefficient again becomes more complex. Given that simple linear sorption equilibrium exists between the diffusing ion and the backfill material, the diffusion coefficient becomes the effective diffusion coefficient and is defined as

$$D' = \frac{D_s}{1+K} \qquad (6.4)$$

where D' = effective diffusion coefficient $(\frac{L^2}{t})$

D_s = whole sediment diffusion coefficient $(\frac{L^2}{t})$

K = linear adsorption constant (m/v)

Care must be taken in the application of these various coefficients. In general, the effective diffusion coefficient is determined in experiments.

Given the above processes, it is useful to know under what condition each is important to radionuclide migration. The importance of dispersion can be ascertained by the determination of the Peclet number which is defined as

$$P_e = \frac{2rU}{D} \qquad (6.5)$$

where P_e = Peclet number

r = bed particle radius L

U = groundwater flow rate $(\frac{L}{t})$

D = coefficient of diffusion $(\frac{L^2}{t})$

For Peclet numbers of less than one, dispersion is considered an insignificant transport process [1,10]. Given a typical clay backfill particle radius of about 3×10^{-3} cm and a diffusion coefficient of 1×10^{-5} cm^2/s, dispersion would only be important at flow rates of greater than 1×10^{-3} cm/s.

As for the relative significance of diffusion and advection, Ahn, Dayal, and Wilke[11] and Nowaks[6] calculated parametrically that at flow rates of less than 1×10^{-7} cm/s, advection had little or no influence upon radionuclide breakthrough through a clay barrier. According to Berner[13], a simple method to assess the relative contributions of advection and diffusion is to use the equation

$$D_s = LU \qquad (6.6)$$

where D_S = whole sediment diffusion coefficient $(\frac{L^2}{t})$

L = migration distance (L)

U = flow rate $(\frac{L}{t})$

If $D_S >> LU$, diffusion is the principal transportation mechanism and if $D_S << LU$, advection is the principal transportation mechanism. In the case where sorption processes are significant, the effective diffusion coefficient should be used. Table 6.1 presents the flow rates and diffusion coefficients where $D_S = LU$, that is, where diffusion contributes to transport as much as advection does. Assuming a typical value of D_S of about 3×10^{-6} cm^2/s, we can conclude from Table 6.1 that for a 30 cm thick backfill bed, diffusion is the dominant transport process for flow rates below 1×10^{-7} cm/s and that for a 100 cm thick bed, diffusion dominates only if the flow is less than 1×10^{-8} cm/s. If advective movement is slightly greater than diffusive movement, it is also apparent that with a larger migration distance involved, advection takes on even greater significance. This information can be of value in simplifying test design and the interpretation of results.

Table 6.1
Flow Rates and Diffusion Coefficients Where
Advection and Diffusion are of Equal Significance(13)

L = 30 cm		L = 100 cm	
D_S (cm^2/s)	U (cm/s)	D_S (cm^2/s)	U (cm/s)
3×10^{-7}	1×10^{-8}	1×10^{-6}	1×10^{-8}
3×10^{-6}	1×10^{-7}	1×10^{-5}	1×10^{-7}
3×10^{-5}	1×10^{-6}	1×10^{-4}	1×10^{-6}
3×10^{-4}	1×10^{-5}	1×10^{-3}	1×10^{-5}
3×10^{-3}	1×10^{-4}	1×10^{-2}	1×10^{-4}

D_S = Whole sediment diffusion coefficient

L = Migration distance (backfill thickness)

U = Flow rate

6.2.2 Retardation Processes

The impact of sorption upon radionuclide transport is of the utmost significance since it represents the primary means by which radionuclide transport is retarded. These reactions include reversible mechanisms such as ion-exchange and adsorption, and irreversible mechanisms such as fixation and precipitation. The importance of these reactions depends directly upon the chemistry of the various radionuclides involved coupled with the repository conditions and the nature of the backfill itself. Non-reactive ions such as tritium will migrate primarily due to diffusion and advection. Migration of univalent fission products will be retarded principally by means of ion-exchange and, in some instances, by the formation of precipitates.[3] Retardation of the multivalent radionuclides represents a more complex situation involving ion-exchange, precipitation, reduction-oxidation, and hydrolysis.[8,14-17] Retardation of radioactive anions has been accomplished by reducing minerals and sulfides.[4] Recent research by Nowak[18] (Sandia) has also indicated reasonable anion adsorption by activated charcoal.

Not all reactions involving radionuclides serve to retard their migration. The results of some research have indicated the formation of highly soluble radionuclide complexes with inorganic ligands such as carbonate and bicarbonate.[3,8,15] Radiocolloid formation has also been demonstrated as a potential transport mechanism.[19] Obviously, these mechanisms would tend to facilitate radionuclide migration.

6.3 Backfill Testing

In the past, the standard means used to evaluate the sorption of radionuclides by a solid has been the system K_d value or equilibrium distribution coefficient. This coefficient is a measure of the partitioning of a radionuclide between solid and liquid phases of a static system. The laboratory measurement of K_d values has been a practical method for qualitative screening the sorptive properties of various candidate backfills. However, this method offers no prospect for evaluating the quantitative response of the backfill in an actual flowing groundwater scenario.

For testing backfill materials, certain information must be determined under conditions which most reasonably simulate anticipated repository conditions. Candidate backfills must be compared with respect to their radionuclide retention characteristics. This type of data on dynamic systems can be obtained by the determination of radionuclide/backfill retardation factors and diffusion coefficients. Also necessary is a method by which backfill performance can be related to regulatory criteria. This need can be fulfilled by utilizing retardation factors and diffusion coefficients in mass-balance models to calculate radionuclide breakthrough times and release rates. These topics are discussed in the following sections.

6.3.1 Repository Conditions and Backfill Characterization

In order to be able to test backfills in the thermal, hydrologic and chemical environments in which they will be required to perform, a thorough

knowledge of the anticipated repository conditions is essential. A list of these factors is given in Table 6.2. Repository conditions are discussed in Chapter 6 of the Task 1 report.[20]

Dependent upon waste type, waste form loading and repository design, temperatures in the backfill can be expected to range from ambient levels to up to 318°C (maximum expected rock temperature, HLW in basalt at 130 Kw/acre) [21]. Such temperatures cannot only influence the near field chemistry with respect to such parameters as pH, Eh and reaction rates, but also the stability of the backfill itself, a topic mentioned earlier. Flow rates, important with respect to the magnitude of advective transport, can vary widely with generic values of hydraulic conductivities (gradient normalized flow rates) for prospective host rocks ranging from 1.4×10^{-12} cm/s [22] for crystalline rock up to about 1.2×10^{-3} cm/s[23] for shale. Groundwater composition and concentrations are known to vary widely[26] and along with pH and Eh are critical factors with respect to radionuclide chemistry and sorptive properties.[3,14,15,24,25]

Table 6.2

Factors Affecting Radionuclide Migration
in Backfill Materials

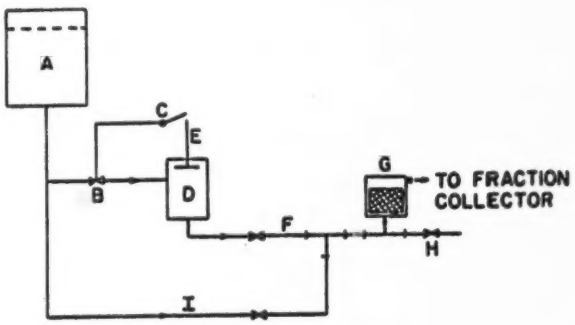
Repository Conditions	Backfill Characteristics
Temperature	Mineralogy
Flow rate	Surface Area
Groundwater Composition and Concentation	Particle Size Distribution
pH	Cation Exchange Capacity
Eh	
Radiation Field	
Presence of Container	
Corrosion Products	

The physical characteristics of the backfill material are important, primarily with regard to the interaction of dissolved radionuclides and the backfill itself. The mineralogy of the backfill in conjunction with knowledge of the test conditions is especially important in order to derive mechanistic and predictive information on such processes as ion-exchange and chemisorption The backfill should be thoroughly characterized with respect to mineralogy, both qualitatively and quantitatively if possible. Information on the cation exchange properties, specific surface area and particle size distribution would be also helpful in assessing surface reactions and potential particle transport.[20,25]

6.3.2 Determination of Retardation Factors

A strictly empirical approach to backfill testing can be taken by utilizing flow through column experiments to determine radionuclide/backfill retardation factors. By monitoring the radionuclide concentrations in the effluent of such tests, the radionuclide retardation characteristics of a backfill under a given set of conditions can be determined. As was mentioned before, this form of test reasonably simulates the hydrologic conditions of a repository, conditions which are well known to influence solute transport through porous media.[29-31] This type of test is in common use in the soil sciences[32-33] and has been used in the nuclear waste disposal field.[3,34]

A typical experimental apparatus is given in Figure 6.2. Such an apparatus is quite versatile enabling the study of such important parameters as flow rate, temperature, groundwater composition, radiation field and so on, so that all of the anticipated repository conditions can be simulated.



FLOW THROUGH COLUMN APPARATUS

A	MAIN RESERVOIR	H	COLUMN CHAMBER DRAIN LINE
B	SOLENOID VALVE	I	BY-PASS LINE
C	MICRO SWITCH	↑	DIRECTION OF WATER MOVEMENT
D	HYDRAULIC HEAD RESEVOIR	⋈	VALVE-ONE WAY
E	FLOAT	⊤	T-CONNECTOR
F	FEED LINE		
G	COLUMN CHAMBER		

Figure 6.2. An example of a flow-through column testing apparatus.[35]

Relyea et al.[24] (PNL) summarized the data required to interpret column experiments. Assuming that the test conditions, groundwater composition, mineralogy etc. are reported and from a knowledge of: bedlength (L), bed radius (r), bed bulk density ($_B$), backfill particle density ($_p$), time (T), volumetric flow rate (Q) and the radionuclide concentration in the effluent versus time, a number of quantities, given in Table 6.3, can be calculated.

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Table 6.3 Calculated Parameters for Column Experiments[24]

Column Volume (V_C) = $\pi r^2 L$

Static Total Porosity (ε) = $1 - \frac{\rho_B}{\rho_p}$

Static Pore Volume = (ε) (V_C)

Pore Water Velocity (v_w) = $\frac{LQ}{\varepsilon V_C}$

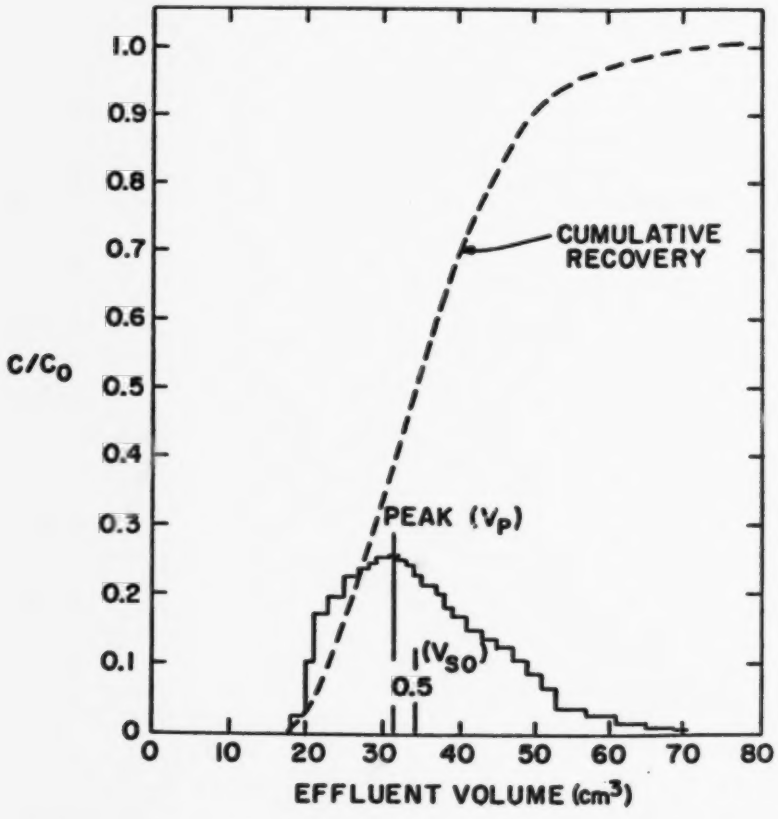

Figure 6.3. An example of a radionuclide breakthrough curve from column testing (pulse addition).[24]

By monitoring the radionuclide concentration in the column effluent an elution curve like that in Figure 6.3 can be developed. In the instance where radionuclides are applied to the column as a pulse, the radionuclide retardation factor can be determined either from equation 6.7 or 6.8 where Vp represents the effluent

$$R_f = \frac{V_p}{\varepsilon V_C} \qquad (6.7)$$

$$R_f = \frac{V_{50}}{\varepsilon V_C} \qquad (6.8)$$

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volume where the peak radionuclide concentation was observed and where V_{50} represents the effluent volume where 50% of the applied radionuclide has eluted. In the cases where the radionuclide is continuously applied to the column, the technique recommended in the interim report[35], the effluent volume corresponding to $C/C_0 = 0.5$ can be substituted for V_P or V_{50}. Here, C equals the effluent radionuclide concentation and C_0 equals the influent radionuclide concentrations.

Ideally V_P and V_{50} should be equal, but as can be seen from Figure 6.3 this is not always the case and the smaller of the values should be used to be conservative. From the perspective of meeting regulatory criteria, breakthrough would probably be defined at a lower radionuclide concentration than those achieved at peak or 50% breakthrough, perhaps at $C/C_0 = 0.10$, 0.05, or 0.01 (10, 5, and 1%, respectively). The volume corresponding to the defined value of breakthrough could then be substituted in the above calculation.

Knowledge of the retardation factor of a backfill/radionuclide system is valuable in that it provides for a quantitative means by which the effectiveness of backfill barriers can be compared. This quantity has also been defined in other ways by other researchers. For example, it has been defined as:

$$R_f = \frac{\nu_w}{\nu_n} \tag{6.9}$$

where ν_w is the water velocity (ν_w from Table 6.3) and ν_n is the radionuclide velocity through the backfill. The retardation factor has also been calculated on the basis of distribution coefficients, but given that backfill will be required to perform in a dynamic situation, it is felt that the means to determine the retardation factor as described above, using column tests, is the most realistic. It should be noted that the value of static porosity can be substituted for with a value for the effective porosity. The effective porosity (ε_D) is the pore volume of the bed actually available for fluid transmission. Due to the existence of isolated pore spaces or dead-end pores, effective porosity is usually less than static porosity. The effective porosity can be determined using a non-sorbing or conservative tracer such as tritium. The volume corresponding to peak breakthrough of tritium is taken as the effective pore volume of the bed. Dividing this volume by the column volume yields the effective porosity. If the peak breakthrough volume of the tritium and its 50% mass breakthrough do not correspond, they should be averaged.

Some controversy does exist about the non-sorbing nature of tracers like tritium or anionic tracers. Relyea et al.[24] point out that tritium is known to exchange with stable hydrogen and can be retarded relative to the groundwater. Anionic tracers can be sorbed by anion exchangers or subjected to anion exclusion. Both effects cause elution of the tracer to be delayed relative to the actual groundwater front. More research is needed in this area but, that lacking, values resulting in conservative estimates of breakthrough should be used.

According to Relyea et al.,[24] when the pore water radionuclide distribution has been established, the retardation factor for the system can be calculated by

$$R_f = \frac{QtL}{X\varepsilon V_c} \qquad (6.10)$$

where X equals the distance the radionuclide front traveled and t equals the time or duration of the experiment. The values Q, L, ε, and V_c are defined as in Table 6.3.

Techniques used in marine geochemical research can be applied to determine the pore water and solid phase distributions of radionuclides, trace elements, or gases within the backfill columns. The backfill columns can be sectioned along their length at discrete intervals and the pore water extracted by means of centrifuging[41] or by pressure squeezing under nitrogen gas.[42] The pore water and solid can then be analyzed by conventional chemical techniques to determine the radionuclide, trace element, or gas distribution within the backfill column. A retardation factor can then be calculated as described above. In addition, a dynamic distribution coefficient can be determined since the concentration of radionuclide in the pore water and on the solid phase will be known.[1] Such procedures should be used routinely in testing, whether or not breakthrough occurred in the test, in order to obtain mechanistic information. The solid phase should also be analyzed after testing for the presence of precipitates and/or authigenic mineral formation.

While dynamic tests are certainly more flexible for approximating expected repository conditions they are also more difficult to execute. Much more attention will need to be given to experimental techniques and equipment design. For example:

- Column edges must be carefully sealed to prevent fluid channeling along the walls.
- Wall effects themselves should be minimized by the use of wide columns.
- Columns should be constructed to allow removal of the backfill in an intact form.
- Radionuclide position in the backfill should be fixed by freezing of the column or the addition of a non-aqueous adhesive.
- Sectioning should be done on a number of vertical and horizontal planes of the column and qualitative autoradiographs should be obtained (see Chapter 4).
- Quantitative information on both γ and α emitters should be possible by acid leaching of each section. Column resolution will thus probably be determined by the sensitivity of the α and γ spectrometry systems.

- Column testing of redox-sensitive elements, such as uranium, plutonium, technicium or neptunium will require close control of the column E_h using for examples reagent buffering techniques. Although these techniques have been used for batch tests, no attempt has been made to use them in columns.

- Given the highly sorptive nature of some ions and the very low flow rates which must be investigated (10^{-8} cm/sec), some accelerated tests appear inevitable. Thus, a series of separate tests should be done to ensure that the retention capacity of the particular column is independent of flow rate, within the accelerated flow range to be investigated.

6.3.3 Determination of Diffusion Coefficients

In the consideration of radionuclide migration, efforts could be directed towards the determination of the diffusion coefficients. In cases where advective radionuclide transport is negligible, transport will be essentially by means of molecular diffusion. Evaluation of such scenarios can be done with knowledge of the diffusion coefficient. A "diffusion only" transport could be envisioned if an extremely low permeability backfill material such as an expandable clay were used.[8] Furthermore, since effective diffusion coefficients, such as those which would be determined by the following methods, include the effects of backfill tortuosity and radionuclide/back-fill sorption, a retardation factor of sorts can be developed for a diffusion transport situation. This could be accomplished by comparing the effective diffusion coefficient of a radionuclide to its simple diffusion coefficient in the appropriate bulk groundwater. Also, these diffusion coefficients, along with the retardation factors derived from column testing, will provide a dynamic data base for use in the quantitative calculation of radionuclide breakthrough and release rates (Section 6.2.4).

A simple means by which diffusion coefficients can be determined is that used by Li and Gregory[37] to study self-diffusion of ions in seawater and Krom and Berner[41] to determine the diffusion coefficients of $PO_4^{\equiv}$, $SO_4^{=}$, and NH_4^{+} in marine sediments. A diagram of the diffusion cell is given in Figure 6.4. The cell is divided into two chambers separated by a filter membrane. For our purposes, backfill samples, homogeneously spiked with different concentrations of the radionuclide under study are placed in each chamber. Alternatively, one chamber can be unspiked. After a given period of time, the chambers are separated and subsampled as a function of depth. These subsamples are then centrifuged to extract their pore water, which is then analyzed to determine the radionuclide concentration profile in each chamber. These profiles are then compared to theoretical curves generated by equation 6.12 in order to determine the best estimate of the diffusion coefficient (see Figure 6.5).

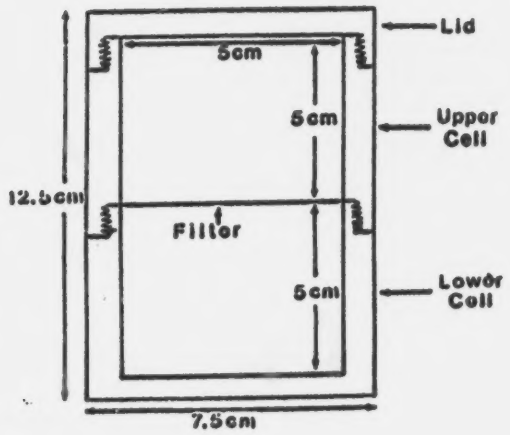

Figure 6.4. Cross-sectional view of cell used for diffusion coefficient determination.(19)

The theory supporting this method assumes that particulate diffusion is negligible and that the interaction between the species under study and the porous media can be represented by linear equilibrium sorption. Thus, the change in concentration versus time of the diffusing species can be represented mathematically by

$$\frac{dC}{dt} = D' \frac{d^2C}{dx^2} \qquad (6.11)$$

where C = concentration in the pore water

D'= effective diffusion coefficient

X = distance

t = time

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The solution of this equation with and for the appropriate initial and boundary conditions is

$$t = 0: \quad x > 0,\ c = c_2 \qquad t > 0: \quad x \to -\infty,\ c \to c_2$$

$$x < 0,\ c = c_1 \qquad\qquad x \to -\infty,\ c \to c_1$$

$$c = c_2 + 1/2(c_1 - c_2)\ \mathrm{erfc}\ [x/(4D't)] \tag{6.12}$$

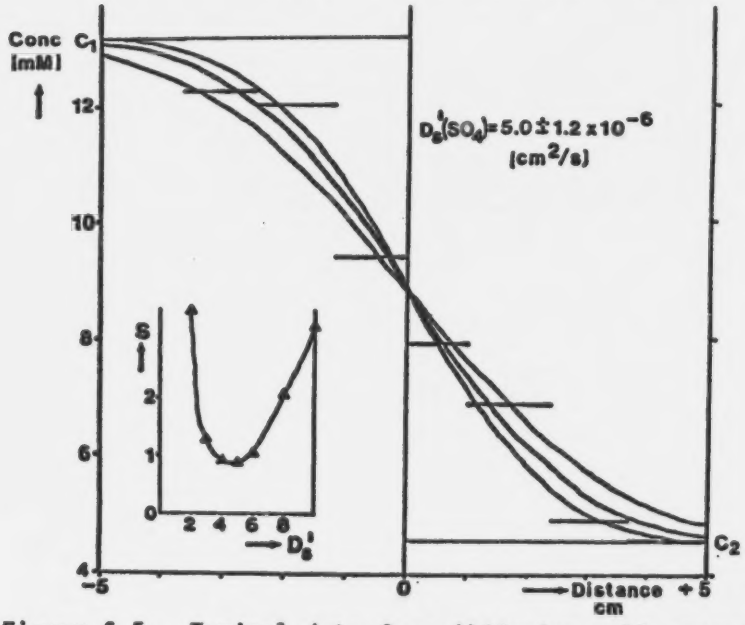

Figure 6.5. Typical data from diffusion cell experiments, horizontal bars represent actual data points while the curves represent theoretical diffusion profiles.[19]

Under circumstances where radionuclide migration can be expected to be very small in the laboratory time frame, as might be the case for some radionuclides under appropriate chemical conditions, the methods described above would be impractical either on analytical grounds in light of the small solution concentration changes involved or the excessive time required to observe diffusion. A technique like that utilized by Fried et al.[2] (ANL) to measure Pu and Am transport in seabed sediments could be utilized. Backfill could be carefully placed in a paraffin cylinder as in Figure 6.6. Then a groundwater or groundwater simulant containing radionuclides would be placed over the backfill and left for an appropriate time period (Fried et al. used 120 days). After this, the groundwater would be removed and the cylinder frozen. Then, the cylinder is sectioned using a refrigerated microtome. The sections are counted and a concentration (or activity) versus depth profile is generated (see Figure 6.7). From these profiles, as with the previous methods, the diffusion coefficient, or in the worst case the maximum diffusion coefficient can be calculated from the solution of equation 6.11 given the appropriate initial and boundary conditions.

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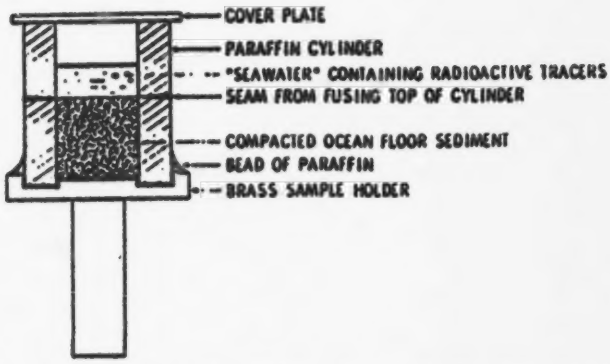

Figure 6.6. Experimental apparatus used to determine diffusion coefficients.(2)

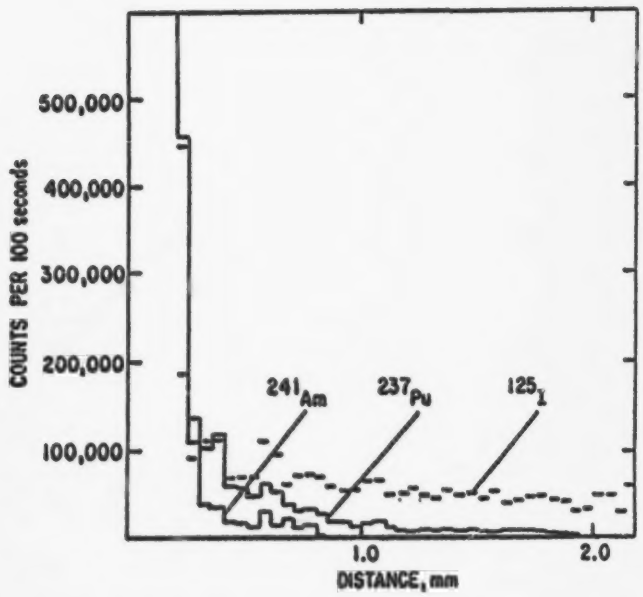

Figure 6.7. Radionuclide distribution curves as obtained using refrigerated microtome method.(2)

Another approach to this problem is to perform column experiments and non-destructively determine the radionuclide profiles within the column. Robbins et al.(36) studied the migration of ^{137}Cs in sediment columns with respect to time by utilizing a collimated NaI detector system to scan the sediment column and thereby develop the radionuclide profile. Curve fitting techniques were applied to the resultant distributions to compare them to

$$A(z,t) = \frac{M}{2\sqrt{\pi D_e t}} e^{-Z^2/4D_e t} \qquad (6.13)$$

where A(z,t) is the activity profile at time t, M is a constant, z is depth in the column and D_e is the effective diffusion coefficient. This type of technique could be used to monitor radionuclide migration through a backfill column as a function of time.

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6.3.4 Quantitative Testing

A more quantitative means by which to test backfill performance is to use mass-balance equations to model the transport and retardation processes involved in radionuclide migration. This type of modeling is the logical "next step" in testing backfill barriers in order to relate their performance to regulatory criteria. The data required to use these models are, primarily, the retardation factor and diffusion coefficients discussed earlier. Many such mass balances exist[45-47] and an example of such a model is the mass balance equation used by Nowak[6] in his evaluation of the performance of a hypothetical montmorillonite clay backfill barrier. The change with respect to time of the quantity of radionuclides within a volume element of the backfill bed can be expressed as

$$\varepsilon \frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} + \varepsilon V_g \frac{\partial C}{\partial x} - \varepsilon D \frac{\partial^2 C}{\partial x^2} = 0 \qquad (6.14)$$

where C = liquid phase concentration

S = solid phase concentration

ε = bed porosity

V_g = groundwater flow rate

X = distance in bed

D_i = combined coefficient of dispersion and diffusion

t = time

The first two terms of the equation describe the mass of the species in question in the liquid and solid phases, respectively. The third term represents radionuclide transport by means of advection, while the fourth term accounts for transport due to dispersion if any, and molecular diffusion. After simplification, this equation was rearranged to

$$\frac{\partial C}{\partial t} + \frac{V_g}{R_f} \frac{\partial C}{\partial x} - \frac{D}{R_f} \frac{\partial^2 C}{\partial x^2} = 0 \qquad (6.15)$$

where $R_f = 1 + \dfrac{\rho_b K_D}{\varepsilon}$

K_D = distribution coefficient

ρ_b = bulk density of bed

Note that R_f values, as determined from the column tests previously discussed, should be used here if they are available for the appropriate conditions.

Nowak subsequently solved this for the case where diffusional transport was occurring in the absence of advection. The solution with the boundary and initial conditions is

$$C = C_o,\ x = 0,\ t > o$$

$$C = 0,\ x > o,\ t = 0$$

$$C/C_o = 1 - \text{erf}\left\{\frac{x}{2\left(\frac{D_f\, t}{\sqrt{2}\, R_f}\right)^{\frac{1}{2}}}\right\} \qquad (6.16)$$

Nowak used the simple diffusion coefficient in his calculation and corrected it to the effective diffusion coefficient by dividing by $\sqrt{2}$, an estimate of tortuosity, and by the retardation factor. Experimentally determined values of the effective diffusion coefficient could be applied here if they are known. Using equation 6.16 then, the breakthrough of a radionuclide through a backfill barrier can be calculated. A similar approach can be taken for the case where advection occurs. Nowak's approach was extended by Ahn, Dayal, and Wilke[11] to demonstrate the effectiveness of backfill in retarding radionuclides in terms of near zero release and 10^{-5}/yr release rate criteria.

By means of such solutions, quantitative data on the breakthrough times and release rates of radionuclides from a backfill can be calculated and provide the information required to demonstrate compliance to regulatory criteria. Data bases of diffusion coefficients and retardation factors can be developed and applied to the mass-balance equation solutions. Efforts along this line would require that these parameters be defined systematically as functions of such variables as temperature, concentration, pressure, groundwater composition, flow rate, etc. for each radionuclide. Furthermore, the mass balance models are versatile; they can be custom tailored to accommodate available data, specifics of experimental and barrier design in order to accommodate various scenarios and extrapolate data to full sized backfill barriers. This should also allow sensitivity studies to determine the effect of uncertainties in the model input parameters.

6.4 Radiation Effects in Sorption Testing

Sorption tests will apply primarily to overpack and host rock materials. Both the solid and liquid phases may be influenced by radiation. Material adjacent to the container may receive gamma doses up to 10^{10} rad in some designs. In others, such as the KBS waste package, the dose will be much lower (Section 5.4).

6.4.1 Ionization in Overpack and Host Rock Materials

Typical backfill materials include clays and zeolites. There is little radiation damage information available on some of these materials.[48] Hydrated minerals such as clays might be modified to some extent by internal radiolysis. (Radiolysis has been observed in concretes, for example.)[49] Should some radiation damage occur, it is not clear that it would be harmful. For example, dehydration may expose more surface area for sorption; our knowledge here is quite incomplete. The basic constituents of many overpack and host rock minerals are oxides which are relatively resistant to bulk ionization damage. Sorption, however, may involve surface effects in aggregate materials. Workers in the USSR[50] have found that radiation influences the surfaces of alumnosilicate minerals, and changes sorption properties. Again, little information is available; however, the effects may be rather modest.

Some radiation damage information has been generated either in actual operations or simulation experiments involving radioactive water cleanup by ion-exchange media.[51-55] In a few cases, beta-gamma doses up to 10^{10} rad or more have been achieved by internal loading (Cs, Sr) or external irradiation. This very limited experience suggests that, indeed, internal radiolysis and/or gas generation may be a consideration depending on radiation dose and moisture content. The effect of radiation on sorptive properties is intriguing: The available information suggests that, due to irradiation or decay heating, the pore structure of heavily loaded zeolites may collapse and tend to fix sorbed radionuclides.[54,55] In effect, since the (beta/gamma) irradiation is produced by the radionuclides themselves, they become "self-trapped".

The possibility of an apparently benefical radiation effect warrants consideration in test development. Whether or not the effect is useful (if in fact it occurs at all) will depend on whether the radionuclides are sorbed before or after the period of intense beta-gamma flux. The internal dose will also depend on the distribution of sorbed radionuclides. Local doses could be quite high if radionuclides are concentrated in the sorption process. Consequently, if the container remains intact during the period of intense beta-gamma decay, it is the sorption properties of externally gamma-irradiated backfill which will be important. (For the bulk of the backfill, under these conditions, the total gamma dose will most probably be lower than that ($>10^{10}$ rad) for which structural changes are inferred in some zeolites). If the container is rapidly breached, it is the effect of internal irradiation on backfill elution properties which must be emphasized. Both conditions, as well as the possibility of gas evolution, should be considered in testing.

As a host medium, rock salt has been studied in some detail.[56,59] This material, however, is not expected to be useful in terms of its sorptive properties. Rather, radiation effects in rock salt may in part establish the environmental conditions under which sorption testing should be carried out. We have previously mentioned radiolysis of rock salt brines.[2] In addition rock salt is, without question, the most susceptible of the candidate host rocks to radiation damage. The extent of the radiation damage is governed by factors such as temperature, radiation dose rate, and total dose.[56,57] Under certain conditions, radiation-induced defect concentrations might approach 0.1% or more in material within about a foot of waste containers.

When irradiated rock salt dissolves in water, gaseous hydrogen and hypochlorite ions are produced, in addition to the usual sodium and chloride ions.[59] The possible presence of these species should be taken into account in assessing the capacity of those materials which might be used as sorption barriers in rock salt. Such barriers, however, might effectively shield the salt from radiation.

6.4.2 Radiolysis Effects on Liquid Media

As in leach and corrosion testing, radiolysis may modify the chemistry of the media which transport radionuclides through the overpack. In certain cases, radiolysis effects are said to increase sorptive capacity slightly. Radiolysis is particularly efficient in liquid media (such as rock salt brines) which contain bromide ion as a scavenger.[60] There is apparently some evidence that radiation effects can influence the oxidation states of plutonium in aqueous solution.[61] The relevance of these and other results toward formulating realistic test conditions needs to be established. For example, valence changes in aqueous species could be overwhelmed by the redox potential of the geochemical environment.

6.5 Conclusions and Recommendations

The emphasis in testing of candidate backfill materials should be placed on dynamic column flow experiments, rather than the static K_d measurements used heavily up to this point. Column tests hold a real prospect for quantitative description of backfill performance which can eventually be linked to the NRC release critereon. More immediately, the column tests will provide a more realistic environment for comparative evaluation of candidate materials. Such tests should be designed to account for the following repository environmental factors: solid/solution ratio, flow rate, groundwater concentration and composition, pH, Eh and the presence of corrosion products.

The pore water chemistry of backfill/radionuclide systems should be examined as a part of all tests. In cases where radionuclide breakthrough cannot be observed in the laboratory time scale, information on pore water chemistry is necessary to determine the rate and extent of radionuclide migration. Regardless of whether radionuclide breakthrough can be observed, analysis of the pore water chemistry can provide information to determine radionuclide partitioning between the solid and liquid phases and can also provide information on such processes as the formation of precipitates and/or authigenic minerals.

Column testing using accelerated flow rates appears inevitable for highly sorptive ions. Separate tests are thus required to explore the effect of flow rate on retention capacity.

The data obtained in the retardation factors and diffusion coefficients of radionuclide/backfill systems appears ammenable to analysis by mass-balance type models. These models, which are sufficiently flexible to study the effects of repository conditions, backfill characteristics and backfill design, can be used to estimate radionuclide breakthrough times and release rates for candidate backfill materials. This quantitative information can then be used

to evaluate backfill performance in terms of the NRC 1000 year containment and 10^{-5}/yr controlled release rate criteria. Sensitivity analysis of such models is important in establishing their credibility.

Finally, tests will also be required to determine the effect of irradiation on backfill performance under repository conditions. These tests should evaluate:

(a) the effect of external gamma irradiation on sorption properties,

(b) the effect of radiation by sorbed nuclides on elution properties,

(c) the nature and extent of radiolytic gas generation from the dry backfill,

(d) the effects of radiolysis of liquid media on the sorptive properties,

(e) the effect of radiation-induced structural changes on backfill permeability.

These evaluations should explicitly consider the fact that, in the repository, the backfill may either be irradiated or called on to perform at elevated temperatures. It should also be determined if radiation effects are sensitive to backfill moisture content or the identity of sorbed species.

6.6 References

1. A. Lerman, Geochemical Processes - Water and Sediment Environments, Chapters 1,2,3,8, (John Wiley and Sons, New York, 1979).

2. S. Fried, A. Friedman, J. Hines, R. Sjoblom, G. Schmitz, and F. Schreiner, "Measurement of Penetration Depths of Plutonium and Americium in Sediment from the Ocean Floor," Scientific Basis for Nuclear Waste Management, Vol. 2, C.M.J. Northrup Jr., Ed., (Plenum Press, New York, 1980), pp. 647-654.

3. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, G. E. Bentley, W. R. Daniels, S. J. DeVilliers, F. D. Lawrence, S. Maestas, P. Q. Oliver, J. L. Thompson, E. N. Vine, K. Wolfsberg, "Laboratory Studies of Radionuclide Distribution Between Selected Groundwater and Geologic Media, Annual Report, October 1, 1978 - September 30, 1979,"Los Alamos National Laboratory Report LA-8088-PR, 1980.

4. R. Strickert, A. M. Friedman, and S. Fried, "The Sorption of Technetium and Iodine Radioisotopes by Various Minerals," Nuclear Technology, 49, 253 (1980).

5. K. L. Erickson, W. E. Seyfried, G. R. Heath, J. L. Krumhansl and V. T. Bowen, "Geochemical Studies Supporting the U.S. Subseabed Disposal Program," Sandia National Laboratory Report, SAND80-1407C, 1980.

6. E. J. Nowak, "The Backfill Barrier as a Component in a Multiple Barrier Nuclear Waste Isolation System," Sandia National Laboratory Report, SAND79-1109, 1980.

7. T. D. Chikalla and J. A. Powell, "Nuclear Waste Management Quarterly Progress Report July through September 1980," Pacific Northwest Laboratory Report, PNL-3000-7, 1980.

8. E. J. Wheelwright, "Development of Backfill Material, in "Nuclear Waste Management Quarterly Progress Report April through June 1980," (A. M. Platt and T. A. Powell, Eds.) Pacific Northwest Laboratory Report, PNL-3000-6, 1980.

9. T. Vermuelen, G. Klein, and N. K. Hiester, "Adsorption and Ion-exchange" in Chemical Engineers Handbook, 5th ed., (R. H. Perry and C. H. Chilton, eds.), (McGraw-Hill, New York, 1973).

10. J. Bear, Dynamics of Fluids in Porous Media, (American Elsevier Environmental Science Series, New York, 1971).

11. T. M. Ahn, R. Dayal, and R. J. Wilke, "Evaluation of Synthetic Zeolites as Backfill in a HLW Repository," Appendix to a letter from D. G. Schweitzer (BNL) to E. A. Wick (NRC), 11/12/80.

12. I. Neretnieks, "Retardation of Escaping Nuclides from a Final Repository," Kaern Braenslesaekerhet, (Sweden) KBS-TR-30, 1977.

13. R. A. Berner, Early Diagenisis - A Theoretical Approach, (Princeton University Press, Princeton, New Jersey, 1979), p. 241.

14. B. Allard, H. Kipatsi, and J. Rydberg, "Sorption of Long-lived Radionuclides in Clay and Rock," Kaern Baernslesaekerhet, (Sweden) KBS-TR-55 (1977).

15. B. Allard, H. Kipatsi, and B. Torstenfelt," Sorption of Long-lived Radionuclides in Clay and Rock - Part 2," Kaern Baernslesaekerhet, (Sweden), KBS-TR-98 (1978).

16. B. M. Crowe, B. P. Bayhurst, P. L. Bussolini, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. E. Goff, G. Heiken, F. O. Lawrence, J. R. Smyth, M. Sykes, J. L. Thompson, E. N. Vine, and K. Wolfsberg, "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1 - September 30, 1979", Los Alamos National Laboratory Report, LA-8152-PR, 1979.

17. B. Allard, G. W. Beall, T. Krajewski, "The Sorption of Activities in Igneous Rocks," Nuclear Technology, 49, 474 (1980).

18. E. J. Nowak, "Backfill Barriers for Nuclear Waste Repositories in Salt," Sandia National Laboratories Report, SAND81-0377A, 1981.

19. G. G. Eichholz, "Subsurface Migrations of Radioactive Waste Materials by Particulate Transport," Abstracts, Waste Rock Interaction Technology Meeting, 13-15 October 1980, Seattle, Washington.

20. R. Dayal, B. S. Lee, R. J. Wilke, K. J. Swyler, P. Soo, T.-M. Ahn, N. S. McIntyre and E. Veakis, "NRC Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria, Task 1: Waste Package Overview, Final Report", BNL-NUREG-27961R (July 1981).

21. U.S. Department of Energy, Final Environmental Impact Statement, Management of Commerically Generated Radioactive Waste, V. 2, DOE/ELIS-0046F 1980.

22. I. W. Marine, "Hydrology of Buried Crystalline Rock at Savannah River Plant near Aiken, South Carolina," Dept. of Energy Report, DOE/SR-WM-79-2, 1979.

23. U.S. Department of Energy, "Technology for Commercial Radioactive Waste Management," Vol. 4, Dept. of Energy Report, DOE/ET-0028 (1979).

24. J. F. Relyea, R. J. Serne, and D. Rai, "Methods for Determining Radionuclide Retardation Factors: Status Report," Pacific Northwest Laboratory Report, PNL-3349 1980.

25. K. S. Czyscinski, K. J. Swyler and C. J. Klamut, "NRC Nuclear Waste Managment Technical Support in the Development of Nuclear Waste Form Criteria - Task 4: Test Development Review," NRC-NUREG-27773 Informal Report, May 1980.

26. R. Dayal, K. J. Swyler and P. Soo, "NRC Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria-Task 1: Waste Package Overview," Brookhaven National Laboratory, BNL-NUREG-27901, Informal Report, June 1980.

27. D. Rai, R. G. Strickert, and J. L. Ryan, "Alpha Radiation Induced Production of HNO_3 During Dissolution of Pu Compounds," Inorganic and Nuclear Chemistry Letters, in press, (1980).

28. B. Allard, H. Kipatsi and J. Rydberg, "Radiolysis of Filling Materials," Kaern Baernslesaekerhet, (Sweden) KBS-TR-56, 1977.

29. J. Rae and D. A. Lever, "Will Diffusive Retention Delay Radionuclide Migation?," AERE Harwell Report, TP853, (1980).

30. R. G. Giast, "Relative Effects of Tortuosity, Electrostatic Attraction, and Increased Viscosity on the Self-diffusion Rates of Cations in Bentunite-Water Systems," in Proceedings of the 1963 International Clay Conference, (Pergamon Press, New York, 1963), pp. 251-259.

31. R. C. Goodknight, W. A. Klickoff and I. Fatt, "Non-steady State Fluid Flow and Diffusion in Porous Media Containing Dead-end Pore Volume," Journal of Physical Chemistry, 64, 1162 (1960).

32. M. Th. Van Genuchten and P. J. Wierenga, "Mass Transfer Studies in Sorbing Porous Media I. Analytical Solutions," Soil Science Society of America Journal, 40, 473, (1976).

33. M. Th. Van Genuchten and P. J. Wierenga, "Mass Transfer Studies in Sorbing Porous Media II. Experimental Evaluation with Tritium," Soil Science Society of America Journal, 41, 272, (1976).

34. S. J. Phillips, "Monitoring and Physical Characterization of Unsaturated Zone Transport," in Nuclear Waste Managment Quarterly Progress Report, April through June 1979 (A.M. Platt and J. A. Powell, Eds.) Pacific Northwest Laboratory Report PNL-3000-2, 1979.

35. K. S. Czyscinski and A. J. Weiss, "Evaluation of Isotope Migration - Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites, Report October 1979 - September 1980.," Brookhaven National Laboratory, BNL-NUREG-51315, 1981.

36. J. A. Robbins, P. L. McCall, J. B. Fisher, and J. R. Krezoski, "Effect of Deposit Feeders on Migration of ^{137}Cs in Lake Sediments," Earth and Planetary Science Letters, 42, 277 (1979).

37. Y. H. Li and S. Gregory, "Diffusion of Ions in Seawater and in Deep Sea Sediments," Geochimica et Cosmochimica Acta, 38, 703 (1974).

38. J. T. Turk, "A Study of Diffusion in Clay-water System by Chemical and Electrical Methods," Ph.D. Thesis, University of San Diego, 111 p., 1976.

39. R. E. McDuff and R. A. Ellis, "Determining Diffusion Coefficients in Marine Sediments: A Laboratory Study of the Validity of Resistivity Techniques," American Journal of Science, 279, 666, (1979).

40. E. J. Wheelwright, "Development of Backfill Materials," in Nuclear Waste Management Quarterly Progress Report July through September 1980, (T. D. Chikalla and J. A. Powell, Eds.), Pacific Northwest Laboratory Report, PNL-3000-7, 1980.

41. M. D. Krom and R. A. Berner, "The Diffusion Coefficients of Sulfate, Ammonium and Phosphate Ions in Anoxic Marine Sediments," Limnology and Oceanography, 25, 327, (1980).

42. W. S. Reeburgh, "An Improved Interstial Water Sampler," Limnology and Oceanography, 12, 163, (1967).

43. I. Neretnieks and C. Skagius, "Diffusivity Measurements in Wet Clay for Na^{+} - Lignosulfonate, Sr^{+2}, and Cs^{+}," Kaern Baernslesaekerhet, (Sweden), KBS-TR-87, 1978.

44. J. Crank, The Mathematics of Diffusion, 2nd Ed. (Clarendon Press, Oxford, 1975).

45. F. Helfferich, Ion Exchange, (McGraw-Hill, New York, 1962).

46. J. F. Relyea, "Diffusion Coefficients and Their Use," Nuclear Technology, 51, 156, (1980).

47. H. Haggblom, "Calculations of Nuclide Migration in Rock and Porous Media Penetrated by Water," Kaern Baernslesakerhet, (Sweden), KBS-TR-52, 1977.

48. G. H. Jenks, "Gamma-Radiation Effects in Geologic Formations of Interest in Waste Disposal: A Review and Analysis of Available Information and Suggestions for Additional Experimentation," Oak Ridge National Laboratory Report, ORNL-TM-4827, 1975.

49. N. E. Bibler, "Radiolytic Gas Production From Concrete Containing Savannah River Plant Waste," Savannah River Laboratory Report DP-1464, 1978.

50. V. I. Spitsyn et al., "Influence of Radiation of the System Liquid Radioactive Wastes - Geologic Formation," in Scientific Basis for Nuclear Waste Management, Vol. I, G. J. McCarthy, Ed. (Plenum Press, N.Y., 1979) pp. 249-256.

51. K.K.S. Pillay, "Radiation Effects on Ion Exchangers Used in Radioactive Waste Management," Pennsylvania State University Report NE/RWM-80-3, 1980.

52. K. Swyler, R. E. Barletta and R. E. Davis, "Review of Recent Studies of the Radiation Induced Behavior of Ion Exchange Media," Brookhaven National Laboratory Report, BNL-NUREG-28682, 1980.

53. R. Fullerton, "The Effect of Gamma Radiation on Clinoptilolide," General Electric Company Report HW-69256, 1961.

54. B. W. Mercer and W. C. Schmidt, "Storage of Long-Lived Fission Products on Alumno-Silicate Zeolites," in Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Waste, USAEC Report LONG-660208, 1966, p. 207.

55. D. Campbell, Oak Ridge National Laboratory, private communication to K. Swyler, Brookhaven National Laboratory, March 27, 1981.

56. K. J. Swyler, L. J. Teutonico and P. W. Levy, Brookhaven National Laboratory, "Radiation Damage Measurements on Rock Salt and Other Minerals for Waste Disposal Applications," Office of Nuclear Waste Isolation Report ONWI/SUB/78/E511-0100-14 1979.

57. L. W. Hobbs, "Application of Transmission Electron Microscopy to Radiation Damage in Ceramics," J. Am. Ceram. Soc. 62, 267 (1979).

58. G. H. Jenks and C. D. Bopp, "Storage and Release of Radiation Energy in Salt in Radioactive Waste Repositories," Oak Ridge National Laboratory Report, ORNL 5058, 1977.

59. G. H. Jenks, E. Sonder, C. D. Bopp and J. R. Walton, "Reaction Products and Stored Energy Released From Irradiated Sodium Chloride by Dissolution and Heating," J. Phys. Chem. 79, 871 (1975).

60. G. H. Jenks, "Radiolysis and Hydrolysis in Salt-Mine-Brines," Oak Ridge National Laboratory Report, ORNL-TM-3717, 1972.

61. S. Fried, A. Friedman, J. C. Sullivan, K. Nash, D. Cohen and R. Sjoblom, "The Radiolytic Oxidation and Reduction of Plutonium," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Ed., (Plenum Press, New York, 1980) pp. 655-664.

7. WHOLE PACKAGE TESTING

7.1 Introduction

In previous chapters the testing and characterization of individual components has been discussed in detail. The likely importance of synergistic effects between components has been outlined, as part of such discussions. The recognition of such effects has led to the recent development of a number of whole package tests which attempt to simulate different failure conditions using accelerated procedures. Another approach to understanding component interaction involves the use of mathematical system modelling. Progress in both experimental and mathematical approaches is reviewed below and an assessment of their relative potential is made.

7.2 Leach Testing

The primary concern in testing the waste package is to determine the radionuclide release rate. The leach test of a proper combination of several components is most widely studied for this purpose. Solution analyses, as well as component characterization, are performed and compared with the results obtained in a single component test.

7.2.1 Experimental Whole Package Tests Under Development

7.2.1.1 Pacific Northwest Laboratory (PNL) Test[1-5]

Cylindrical minicanisters of uranium doped 76-68 glass were prepared by pouring molten glass into 3.81-cm long and 1.27-cm I.D. 304 stainless steel tubes. A slit about 0.32-cm wide, was cut through the canister wall in the axial direction exposing the glass to simulate a fracture. A pellet of glass surrounded by a rim from the canister tube was cut and exposed at one open end of the canister. A rock wafer rested loosely on the exposed glass surface and rock powder (<200 mesh) filled the rest of the space. Various rock types used include basalt, granite, quartz and monzonite (Figure 7.1). About 50 mL of DI water was added to the granite and basalt packages and about 50 mL of salt brine was added to the salt package. The test vessels are either autoclaves or Teflon lined acid digestion bombs. The capacity of a digestion bomb is 125 mL as compared to 850 mL for an autoclave. The temperature (250° or 150°C) and pressure (600 psig for the digestion bomb and 2000 psig for the autoclave) are controlled in the vessel and the tests are conducted for four to six weeks.

Among several options, this design is the closest to the concept of a penetrated or failed waste package, though it is the most expensive. However, control of variables is, as yet, poor and factors such as crack surface area and dissolved oxygen concentration will require better definition in future work.

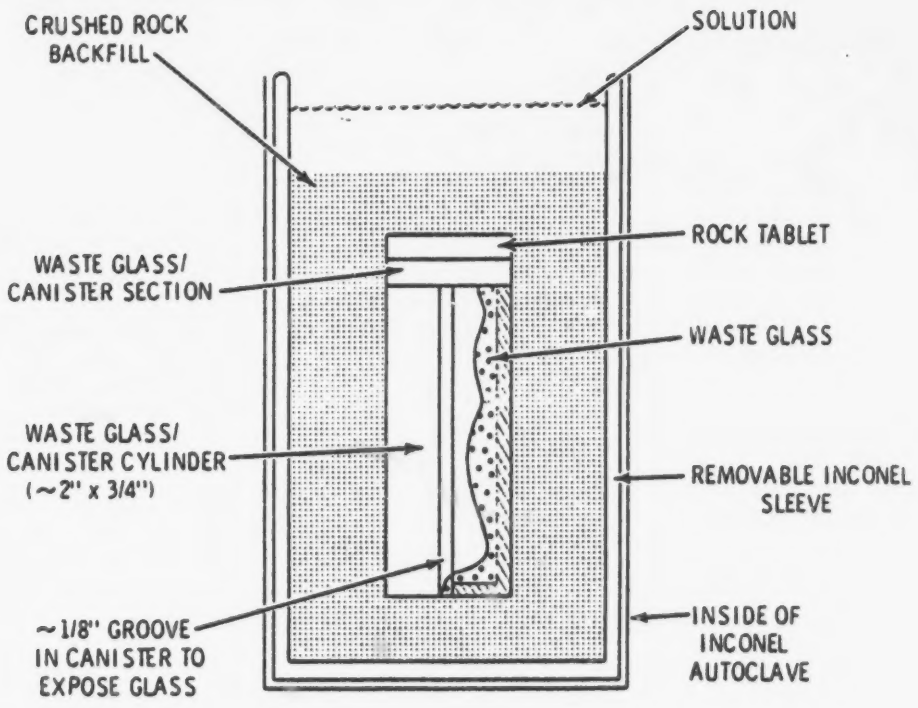

Figure 7.1. Schematic of PNL test package assembly used in autoclave tests.[2]

7.2.1.2 Lawrence Livermore Laboratory (LLL) Test

LLL has designed a continuous flow test that incorporates rock material and waste glass beads.[6,7] Figure 7.2 is a schematic representation of the design which emphasizes the waste/rock interaction. Three flow cells designed for this test were constructed with aspect ratios of 0.1:1, 0.25:1, and 0.4:1, and with a cell length of 9.5 cm. Water was pumped through the cells until the whole system was full of water and free of air bubbles. The inlet tube was then placed in a vessel containing water colored with dark green dye. The system was allowed to pump and the character of the interface between the clear and colored water was observed as a function of time. Experiments were run at volume flow rates of 114 and 13 mL/day.

The test is a fundamental design for waste/rock interaction eliminating complications arising from the multicomponents' interaction, as a first approach to understanding the interaction mechanisms. Variables, such as temperature and pressure, are not controllable. However, the flow rate control is an advantage over the static test.

7.2.1.3 Hanford Test[8-11]

The Basalt Waste Isolation Project of Rockwell Hanford Operations has initiated the package design under both the normal, foreseeable condition and

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under worst case circumstances. Emphasis is given to the reaction of nuclear waste materials with water alone and with water and basalt. Crushed simulated waste and intimate mixtures of crushed simulated waste and basalt were reacted in autoclaves with water at temperatures up to 300°C and a pressure of 300 bars. Simulated spent fuel and simulated supercalcine (SPC-4) and 76-68 glass were used in the presence of basalt. Eh and pH were controlled. This is basically a static test designed, like the LLL test, for a fundamental understanding of waste/rock interaction, but the Hanford test is static and hydrothermal while the LLL test uses flow and ambient conditions.

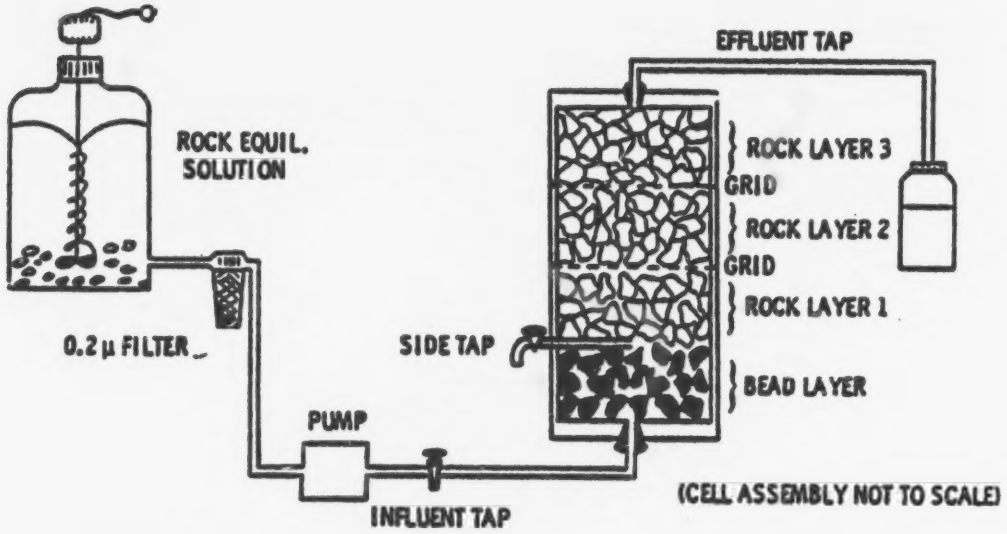

Figure 7.2. Proposed LLL design for continuous flow test incorporating rock media.[7]

7.2.1.4 Pennsylvania State University (PSU) Test

For this waste/rock interaction study[12-17] -200 mesh powder of waste form and rock were mixed with water. Chunks (-6+10 mesh) of both solids in approximately equal masses were also tested. Each test was performed over several months in a sealed gold capsule contained in an autoclave or a cold seal pressure vessel. Test temperatures are up to 400°C and pressures to 300 bars. The waste forms used were 76-68 glass, prototype ceramic (SPC-2), simulated spent fuel, and a raw pw 7-a calcine; the types of rock include basalt, shale and salt.

Like the Hanford test this is a static hydrothermal test designed to obtain basic understanding of waste/rock interactions.

PSU[17-19] extended the above design to include a metal strip such as mild steel, stainless steel, Zircaloy and copper inside a waste/rock mixture.

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The schematics are shown in Figure 7.3. Recently PSU also has begun to develop a flow-through system.

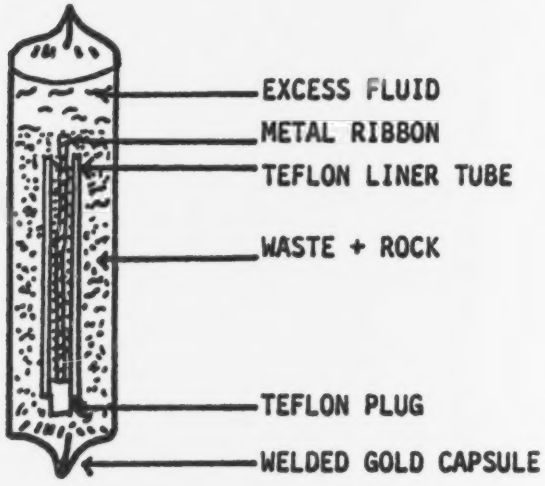

Figure 7.3. PSU experimental capsule for waste-rock canister metal experiments.[7]

7.2.1.5 Other Whole Package Tests

Hench et al.[20] have designed a Teflon corrosion cell which is hollowed out and covered with upper and bottom hoods composed of waste form, canister or rock materials. A static test with leachant inside the hollowed-out section permits the study of synergistic interactions between components.

7.2.2 Solution Analysis and Component Characterization

Standard techniques used in single component leach tests are similarly used for the solution analysis as well as the component characterization in the waste package tests. It is particularly important in the package test:

- to identify the alteration products resulting from the reaction between components. The alteration products are either in the solution as precipitates or solid chunks, or adhere to the solid surface,
- to identify the ion migration from one component to another,
- to subsequently correlate the results from the multicomponent leach rate to the single component leach rate.

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Currently, the U.S.G.S.[21-24] is also planning to study the salt-brine-waste-container interactions. However, no details of the design have yet been reported.

The standard techniques used in single component tests include atomic absorption and emission spectroscopy, inductive coupled plasma spectroscopy, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, and X-ray photoelectron spectroscopy. The detailed evaluation of these techniques is found in Chapter 4.

7.2.3 Variables

7.2.3.1 Components

Each component of the package may affect the observed ion specific leach rate independently. For instance, in the PNL package test,[2] the backfill materials, basalt and granite, retarded the Si, Na and Cs release. However, basalt was found to retard Si and Na release more effectively than granite, while granite retards Cs release more effectively. Figures 7.4 and 7.5 illustrate this behavior. Attempts are being made to correlate such behavior with the nature of the alteration products.

For instance, the presence of basalt affects the suppression of uranium leaching in different ways depending on the types of waste form. In simulated spent fuel, the suppression is obtained by the UO_2 reprecipitation from the dissolved uranium while the formation of pollucite and powellite are responsible for the suppression in the simulated supercalcine.

No comprehensive understanding is available yet for the correlation of alteration product behavior or the interdiffusion of ions between components to the ion specific leach rate. Especially, the role of container materials is rarely understood. Further, basic understanding is largely missing for the role of specific ions of the solution in the solid dissolution. It may be premature to understand the reaction of solution ions and solid in whole package testing, since the understanding of the reaction is not comprehensive even in the single component testing.

As in the single component test, most leach data typically show high leach rates for the initial portion of the test, followed by a more gradual decrease. However, some exceptions are also observed as in the Cs leach in the presence of granite and basalt (Fig. 7.5). Information on the long-term behavior in the leach test may explain this anomaly. No such data on long-term durability are currently available.

7.2.3.2 Temperature

Increased temperature generally increases the leach rate.[2] The increasing rate of leaching depends on the type of component present. For instance, Si release is more pronounced in basalt than in granite when temperatures change from 150° to 250°C.[2]

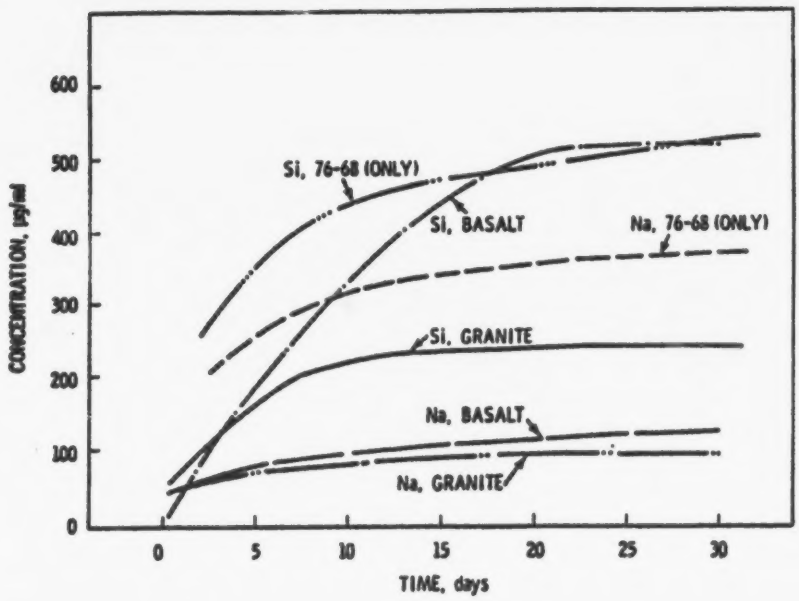

Figure 7.4. Sodium and silicon solution concentrations as a function of time for PNL waste package tests compared with 76-68 glass without rock media present.(3)

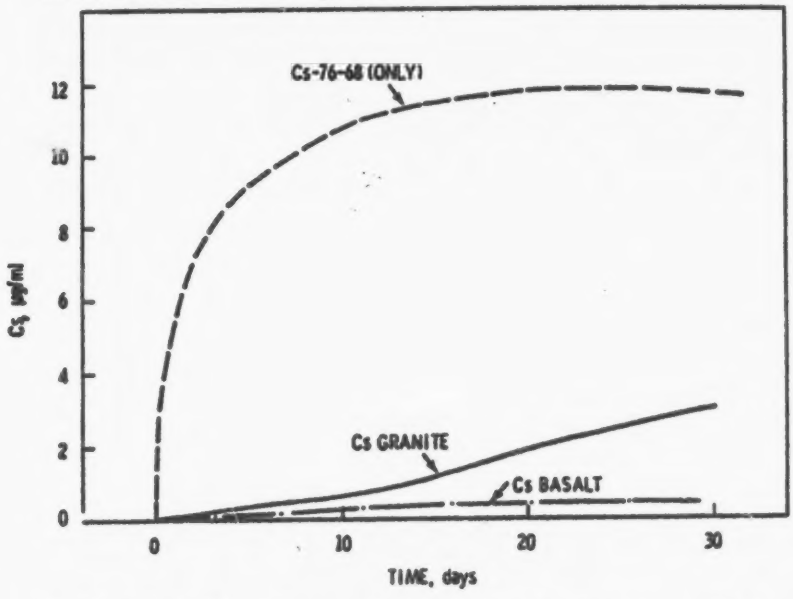

Figure 7.5. Cesium solution concentrations as a function of time for PNL waste package tests compared with 76-68 glass without the presence of rock media.(3)

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Temperature is one of the most effective methods used in an accelerated test provided the leach mechanism does not change upon temperature variation. Understanding the temperature effect, therefore, is one of the ultimate goals of whole package testing.

7.2.3.3 Pressure

Pressure effects have been studied along with elevated temperatures to simulate a hydrothermal environment. Quantitative data for the pressure effect alone are not available. However, it is considered that pressure determines the equilibrium phase of the alteration product or the steady-state ion migration character. Therefore, the pressure indirectly affects the overall leach rate.

7.2.3.4 Aqueous Environment

It is well known that certain of solution ions affect the ion specific leach rate in single component testing. In multicomponent testing similar effects are observed. One example is shown in Table 7.1[3] obtained from PNL tests for a granite matrix. However, there is no systematic information on the role of the modified solution chemistry in the leach reaction. Likewise, the effects of pH and Eh are rarely reported systematically. One probable reason for this is the complications arising from the multicomponent system.

Table 7.1

Increase in Leaching from 25° to 75°C from PNL Tests in Various Aqueous Environments. Shown is the Ratio of Fraction Released at 75° to 25°C at 341 Days.[3]

	Element			
Leachate	B	Ca	Na	Si
Brine	3	a	--	4.5
Bicarbonate	25	3	--	15
Deionized water	34	4	25.5	18

[a]Not determined because of high background in initial leach solutions.

7.2.3.5 Other Variables

Several investigations have confirmed that the ratio of solid surface area to solution volume increases the leach rate following a linear law in a single component test. However, the definition of the surface area has been very ambiguous. For example, internal surfaces in cracks contribute to the overall mass release less effectively than the external surface. Also, in powdered samples, there is a tendency toward setting up heterogeneous corrosion cells by the concentration of fine particles around larger particles leading to an accelerated leach rate. In whole package testing these complications are more significant since the test package design includes crushed

sample or simulated cracked sample. Because of these complications, there is a tendency to use the ratio of solution to solid mass more frequently.[2] However, no systematic data are available as yet on the effect of mass ratio.

LLL and PSU are currently carrying out flow tests to simulate repository flow conditions, as described in Sections 2.1.2 and 2.1.4. Since the flow rate affects the solution pH, saturation of the solution and erosion, even in a single component system, it is premature to state any conclusive flow rate effect yet without an experimental data base in whole package testing.

7.2.4 Summary of the Accelerated Test Method

A common trend is evident in all the package tests reviewed above. They are directed toward understanding synergistic effects using accelerated conditions. As in the single component test, a number of experimental variables are used for acceleration including temperature, pressure, solution concentration, exposed surface area of solid, and flow rate. However, all the efforts are directed toward clarifying the leach mechanism involved in the whole package testing. Therefore, it is quite premature to assess the package performance over geological time and determine the ability of the package to meet NRC criteria until extensive and reliable data are available with a reasonable understanding of the mechanisms involved.

7.3 Quality Assurance of the Waste Package

Before the whole package is emplaced in the underground facility, it should qualify as a standardized truck cask transportable package. Several quality assurance tests are reviewed briefly based on the recent development of standard test methods for the package encapsulating spent fuel light water reactor fuel assemblies and HLW by Westinghouse Advanced Energy Systems Division.[25]

- Drop testing: All canisters containing fuel assemblies or HLW should meet the criteria of maintaining structural integrity and not leaking in excess of 1×10^{-5} scc/sec (helium) after a drop test at the height of 9.1 meters.

- Seismic testing: The package must survive a seismic event of 0.7 g maximum horizontal earth motion. For the simulation of seismic motion, a fixture simulating the EMAD Lag Storage Pit Seismic Restraint is used.

- Welding capability testing: The autogeneous plasma arc welding is the best option.

The quality assurance test is for complete handling, sealing and transportation, to ensure safety from accidents through a design life of 10 years. The design for such a short period in the assurance of the package is relatively easy compared to the performance assessment of the package after emplacement. A little more effort is needed to complete the criteria for the

quality assurance test. Long-term testings over several years are such examples.

7.4 Mathematical Assessment

From our view of the experimental whole package test, we have found that it is premature to draw any reasonable conclusion for the performance assessment of the waste package over geological time. Inevitably, such an assessment will require mathematical analysis of the test data according to a given prescription or model.

The mathematical assessment of the waste packages is a part of waste isolation performance assessment[26,27] which can be accomplished in four parts: near-field scenario analysis, near-field consequence analysis, far-field scenario analysis, and far-field consequence analysis. Scenario analyses are based on the simulation of isolation intrusion, while consequence analyses are based on the simulation of release and transport of radionuclides from the repository. Since NRC efforts are given to waste package development, our review will concentrate on near-field analyses.

A model for barrier performance was completed by workers at SAI[28-30] and the computer code was made operational. The model described conduction heat transfer, uniform corrosion, and mechanical stress for assumed scenarios in which repositories were saturated with groundwater. It pictures the barrier package as a series of cylindrical layers. Each layer consists of a solid wall and a loose layer such as backfill or filler. The solid wall can be composed of one or two materials. The progression of events toward initial release is modeled as successive failures of the layers from the outside toward the inside. Once the solid wall container fails, leakage begins. If a migration barrier is present, a suitable delay time is introduced. Flow diagrams of the model are shown in Figure 7.6 where the calculation of the mass release is based on the experimental data. Calculation will give a reasonable upper and lower board assessment of the near-field scenario and its consequence analysis within a limited experimental data base over geological time periods. Also, the results will be used in selecting the best materials of each component from various candidates. A similar model, the multiple barrier model, was developed by Los Alamos[31] and Rockwell Hanford[32]. This model has some additional input parameters such as ion exchange process. Basic input parameters are again based on the experimental data. Figure 7.7 is a schematic of their model. In the above study of two independent working groups, however, there are many uncertainties, e.g., catastrophic failure or synergistic effects between components, which may need the probabilistic description to the present model for a more realistic assessment with the limited experimental data.

The probabilistic approach was pursued by Pritzker and Gassmann[33] to calculate the overall probability of repository release from individual barrier failure. The system they assumed consists of (a) an isolating medium which prevents groundwater penetration, (b) a waste container, (c) a waste form, and (d) the geologic structure between repository and biosphere. Barrier (a) seems to be equivalent to backfill and overpack. For each barrier,

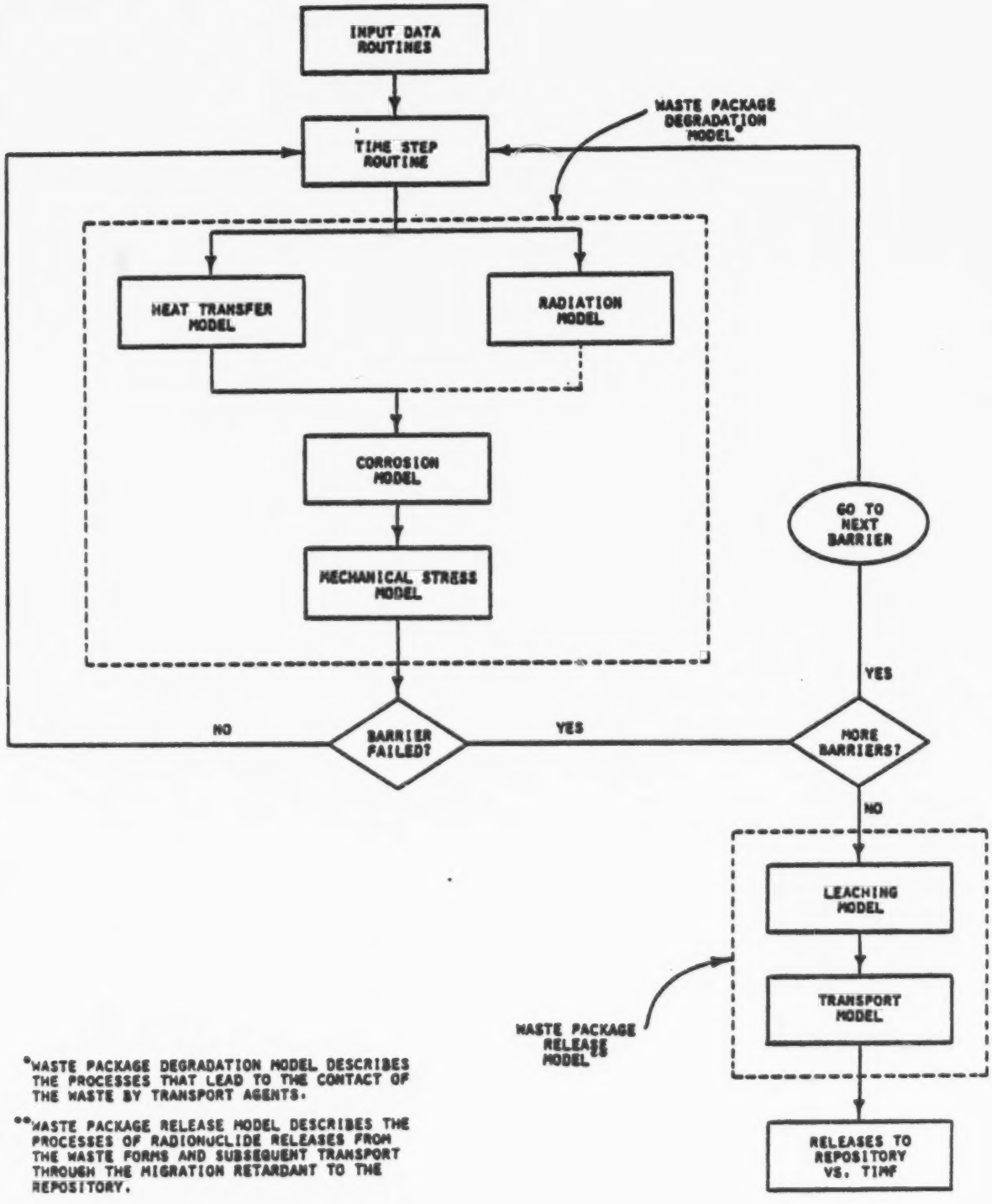
INPUT DATA ROUTINES
TIME STEP ROUTINE
WASTE PACKAGE DEGRADATION MODEL*
HEAT TRANSFER MODEL
RADIATION MODEL
CORROSION MODEL
MECHANICAL STRESS MODEL
BARRIER FAILED?
NO
YES
GO TO NEXT BARRIER
YES
MORE BARRIERS?
NO
LEACHING MODEL
TRANSPORT MODEL
WASTE PACKAGE RELEASE MODEL**
RELEASES TO REPOSITORY VS. TIME
*WASTE PACKAGE DEGRADATION MODEL DESCRIBES THE PROCESSES THAT LEAD TO THE CONTACT OF THE WASTE BY TRANSPORT AGENTS.
**WASTE PACKAGE RELEASE MODEL DESCRIBES THE PROCESSES OF RADIONUCLIDE RELEASES FROM THE WASTE FORMS AND SUBSEQUENT TRANSPORT THROUGH THE MIGRATION RETARDANT TO THE REPOSITORY.

Figure 7.6. Waste package degradation and release model of SAI.[28-30]

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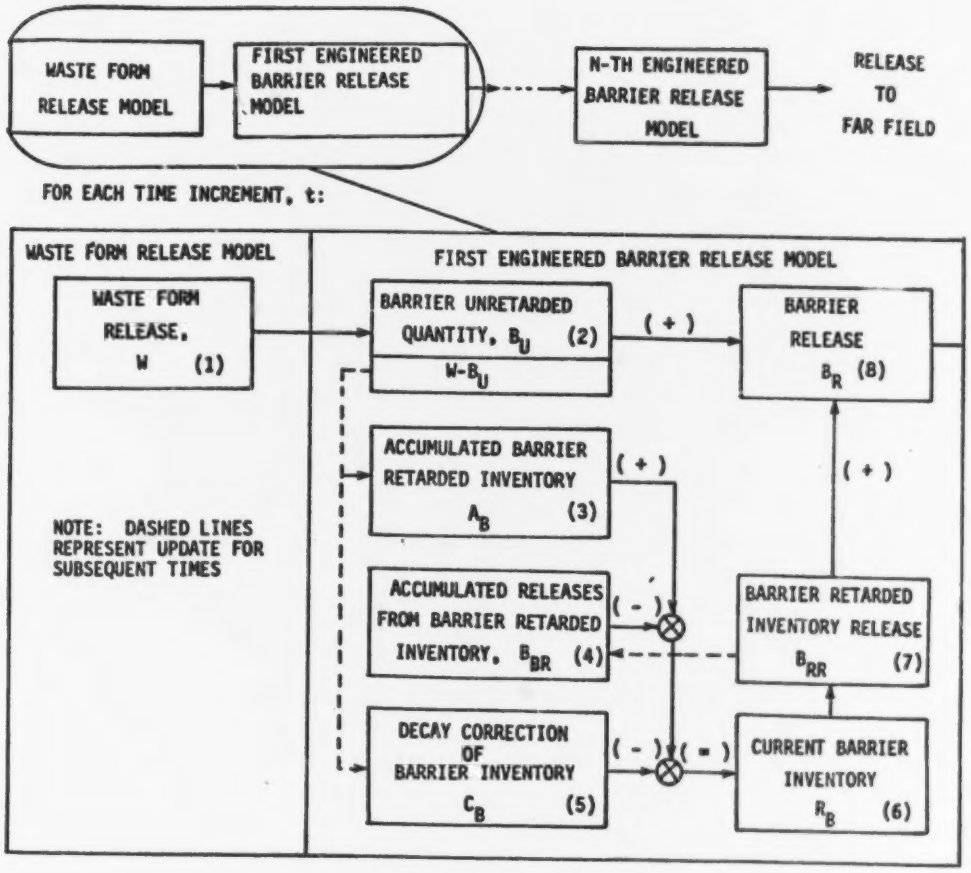
WASTE FORM RELEASE MODEL
FIRST ENGINEERED BARRIER RELEASE MODEL
N-TH ENGINEERED BARRIER RELEASE MODEL
RELEASE TO FAR FIELD
FOR EACH TIME INCREMENT, t:
WASTE FORM RELEASE MODEL
WASTE FORM RELEASE, W (1)
NOTE: DASHED LINES REPRESENT UPDATE FOR SUBSEQUENT TIMES
FIRST ENGINEERED BARRIER RELEASE MODEL
BARRIER UNRETARDED QUANTITY, B_U (2)
W-B_U
BARRIER RELEASE B_R (8)
ACCUMULATED BARRIER RETARDED INVENTORY A_B (3)
ACCUMULATED RELEASES FROM BARRIER RETARDED INVENTORY, B_{BR} (4)
BARRIER RETARDED INVENTORY RELEASE B_{RR} (7)
DECAY CORRECTION OF BARRIER INVENTORY C_B (5)
CURRENT BARRIER INVENTORY R_B (6)
(+)
(-)
(=)

(1) W obtained from waste form leaching model

(2) $B_U = W * F_B$, where F_B is fraction unretarded by barrier

(3) $A_B = \sum_{i=1}^{t-1} (W_i - B_{Ui})$

(4) $B_{BR} = \sum_{i=1}^{t-1} B_{RRi}$

(5) $C_B = \sum_{j=1}^{t-1} \sum_{i=j}^{t-1} (W_j - B_{Uj}) * (1 - \exp(-\lambda * (T_i - T_{(i-1)})))$, where T = TIME

(6) $R_B = A_B - B_{BR} - C_B$

(7) $B_{RR} = R_B * F_R$, where F_R is barrier release fraction

(8) $B_R = B_U + B_{RR}$

Figure 7.7. Conceptual multiple barrier model.(31)

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the time-to-failure is considered as a random variable with a probability density function. The overall repository failure is obtained by summing each part. The calculation seems to apply to predicting the statistical behavior of a large number of repositories. This prescription for "summing the parts" is admittedly oversimplified. The major shortfall is the lack of experimental support in the assessment of each component failure. Perhaps the probability density function for each barrier needs to be experimentally determined by single component or whole package testing.

From the above, we find that the analytical assessment is very useful from the practical viewpoint. A conservative assessment probably can be used as a criterion for licensing procedures. Also, it is advantageous to the waste package design to select the best material for each barrier or the best combination of each component. For this purpose, it is suggested that the two approaches are complementary to each other. The SAI method needs to incorporate the probabilistic prescription, while the probabilistic approach by Pritzker and Gassmann should include the experimental data base.

7.5 Conclusions and Recommendations

The prime concern of the experimental study is to investigate the synergistic effects between components while the analytical study is focused on developing methods of assessing overall waste release over geological times. Both studies are somewhat complementary to each other, and the ultimate goal will be to establish a combined method for a more realistic performance assessment of waste packages.

Basically, two different types of package tests are reported. The PNL test is the closest to the penetrated or failed package, among several options being evaluated. The rest of the package tests are designed for a fundamental understanding of the interaction between two components such as waste/rock. It may or may not include the controls of flow rate and hydrothermal conditions. Although the design is easy to control, it is too simple to be called a failed package.

The whole package tests have somewhat different controlling variables and different behavioral effects when compared to those in the component tests. Characterization of the alteration products and ionic migration at the interface between components is particularly important since the results may explain the leach rate changes of the waste form in the presence of other components. Also important is the mass ratio of solution to solid as a substitute for the ratio of surface area of solid to solution volume probably because of the complexity arising from the extensive use of powder samples.

The characterization of solid and solution is performed in various ways after leach testing. Various techniques for chemical and microstructural analyses have been briefly reviewed.

It must be realized that experimental data will give only limited information on the performance of whole package over geological time. They are qualitative tests, particularly suited to understanding synergistic

effects between components. For quantitative assessment, mathematical modeling is the inevitable choice.

Quality assurance of the waste package is another aspect of package testing. This is aimed at the standardization of test methods for safe handling, transportation and emplacement of the package in underground facilities. The tests include drop testing, seismic testing, and weld testing. There are no technical difficulties with these standardized procedures.

On the basis of the above review, we recommend several areas of research as listed below:

- Design more realistic failed packages. One example may include a container breached by accelerated local corrosion techniques.
- Include various combinations of materials in binary interaction testing. Data are especially lacking for waste form/container, container/backfill, and backfill/host rock.
- Study systematically the correlation of ion-specific leach data to the characterization of alteration products and ionic migration in solids.
- Study systematically the effects of variables, particularly those such as temperature, solution Eh and pH.
- Develop a comprehensive model for the analytic assessment of waste package performance over geological time incorporating both the experimental data and the probabilistic descriptions.

7.6 References

1. A. M. Platt and J. A. Powell, "Nuclear Waste Management Quarterly Progress Report, October-December 1979, Waste/Rock Interaction Technology," Pacific Northwest Laboratory Report No. PNL-3000-4, 1980.
2. J. W. Shade and D. J. Bradley, "Initial Waste Package Interaction Test: Status Report," Pacific Northwest Laboratory Report No. PNL-3559, 1980.
3. A. M. Platt and J. A. Powell, "Waste/Rock Interaction Technology," in Nuclear Waste Management Quarterly Progress Report, April-June 1980, Pacific Northwest Laboratory Report No. PNL-3000-6, 1980.
4. J. W. Shade and D. J. Bradley, "Joint PNL-WIPP NLW Total System Test, Proceedings of ONWI Meeting," Office of Nuclear Waste Isolation Report No. ONWI-212, 1980, p. 171.
5. R. J. Serne, "Waste/Rock Interactions Technology Program (WRIT)" in Technical Progress Report for the Quarter 1 January - 31 March, 1980, Office of Nuclear Waste Isolation Report No. ONWI-9(2), 1980.

6. A. Brandstetter, M. A. Harwell, G. L. Benson, D. J. Bradley, J. R. Raymond and R. J. Serne, "Waste Isolation Safety ASsessment Program," in Technical Progress Report for the Quarter 1 July - 30 September, 1979, Office of Nuclear Waste Isolation Report No. ONWI-9(4), 1980.

7. R. J. Serne, "Waste/Rock Interactions Technology Program (WRIT)," in Technical Progress Report for the Quarter 1 October - 21 December, 1979, Office of Nuclear Waste Isolation Report No. ONWI-9(1), 1979.

8. M. J. Smith, "Waste Package Development for a Nuclear Waste Repository in Basalt," ibid. Ref. 6, p. 240.

9. M. J. Smith, "Waste Package Development for a Nuclear Waste Repository in Basalt," Rockwell Hanford Operation Report, RHO-BWI-SA-97, 1980.

10. W. E. Coons, "Reactions of Spent Fuel and Reprocessing Waste Forms With Water in the the Presence of Basalt," D'Appolonia Report to BWIP, Albuquerque, New Mexico, 1980.

11. W. E. Coons and E. S. Patera, Jr., "Reactions of Spent Fuel and Reprocessing Waste Forms With Water in the Presence of Basalt," ibid. Ref. 6, p. 121.

12. B. E. Scheetz, S. Komarneni, D. K. Smith, C. A. F. Anderson, S. D. Atkinson and G. J. McCarthy, "Hydrothermal Interaction of Simulated Nuclear Waste Glass in the Presence of Basalt," in Scientific Basis for Nuclear Waste Management, Vol. 2, Ed. by C. J. M. Northrup, Jr., Plenum Press, 1979, p. 207.

13. B. E. Scheetz, S. Komarneni, D. K. Smith and C. A. F. Anderson, "Hydrothermal Interaction of a Ceramic Waste Form With Basalt," in Proceedings of Alternative Nuclear Waste Forms and Interactions in Geologic Media - A Workshop, ORNL Conference, Gatlinburg, Tennessee, (1980).

14. G. J. McCarthy, S. Komarneni, B. E. Scheetz and W. B. White, "Hydrothermal Reactivity of Simulated Nuclear Waste Forms and Waste Catalyzed Waste/Rock Interactions," in Scientific Basis for Nuclear Waste Management, Vol. 1, Ed. by G. J. McCarthy, Plenum Press, (1978), p. 329.

15. W. B. White and J. V. Biggers, "The Chemistry and Physics of Nuclear Waste/Rock Interactions" in Technical Progress Report for the Quarter 1 April - 30 June 1979, ONWI-9(3), 1979.

16. W. B. White and J. V. Biggers, "The Chemistry and Physics of Nuclear Waste/Rock Interactions," ibid. Ref. 8, p. 128.

17. W. B. White, W. P. Freeborn, S. Komarneni, "Chemical Interactions of Shale Rock, Prototype Waste Forms, and Prototype Canister Metals in a Simulated Wet Repository Environment," ibid. Ref. 6, p. 127.

18. W. B. White and J. V. Biggers, "The Chemistry and Physics of Nuclear Waste/Rock Interactions," ibid. Ref. 9, p. 114.

19. W. B. White and J. V. Biggers, "The Chemistry and Physics of Nuclear Waste/Rock Interactions," ibid. Ref. 7, p. 113.

20. L. L. Hench, D. E. Clark and E. L. Yen-Bower, "Surface Leaching of Glasses and Glass-Ceramics" in Proceedings of the Conference on High Level Radioactive Solid Waste Forms, Ed. L. A. Casey, Denver, Colorado, (1978).

21. M. A. Clynne, "Salt-Brine-Waste-Canister Interactions," ibid. Ref. 9, p. 142.

22. M. A. Clynne and I. M. Chou, "Salt-Brine-Waste-Canister Interactions," ibid. Ref. 7, p. 137.

23. R. W. Potter II, "Salt-Brine-Waste-Canister Interactions," ibid. Ref. 17, p. 120.

24. R. W. Potter II, "Salt-Brine-Waste-Canister Interactions," ibid. Ref. 8, p. 152.

25. R. J. Bahorich, D. F. Moran and R. J. Steffen, "Experimental Demonstration Package Program," ibid., Reference 4, p. 235.

26. Office of Nuclear Waste Isolation, "Earth Science Technical Plan for Disposal of Radioactive Waste in a Mined Repository," Department of Energy DOE/TIC-11033 (Draft), (April 1980).

27. B. J. Wood, "Estimation of Waste Package Performance Requirements for a Nuclear Waste Repository in Basalt," ibid. Ref. 6, p. 335.

28. D. H. Lester, "System Study on Engineered Barriers: Barrier Performance Analysis," ibid. Ref. 8, p. 270.

29. D. H. Lester, "System Study on Engineered Barriers: Barrier Performance Analysis," ibid. Ref. 17, p. 251.

30. D. H. Lester, R. T. Stula, B. E. Kirsteim, and T. E. Albert, "Waste Package Performance Analysis," ibid. Ref. 6, p. 328.

31. B. J. Wood, "Estimation of Waste Package Performance Requirements for a Nuclear Waste Repository in Basalt," Rockwell Hanford Report RHO-BWI-57-10, 1980.

32. S. E. Logan and R. B. Lantz, "Long Term Risk Assessment," in Basalt Waste Isolation Project Annual Report - Fiscal Year 1979, Rockwell Hanford Report RHO-BWI-79-100, 1979.

33. A. Pritzker and J. Gassmann, "Application of Simplified Reliability Methods for Risk Assessment of Nuclear Waste Repositories," Nucl. Tech. 48, 289, 1980.

8. SUMMARY OF CONCLUSIONS

8.1 Waste Form Testing and Characterization

(a) The MCC has, since its inception, moved to improve confidence in all types of testing methods related to high level waste disposal. Of particular note are the series of waste form leaching tests designed to compare different waste forms under a comprehensive set of geological conditions.

(b) Eventually, however, waste form leaching must be understood on a mechanistic basis. Without a fundamental understanding of the leaching processes, no confident prediction of long-term behavior can be made. Knowledge of leaching mechanisms is also essential to the competent application of any type of accelerated test. Mechanistic studies of multi-phase waste forms will require particularly detailed attention since each phase will respond in a different way and will likely interact with neighboring phases during leaching.

(c) In future leaching tests to be specified by MCC, much greater emphasis should be placed on characterization of the waste form itself during and following a leaching experiment. This will result in more understanding of the mechanisms causing radionuclide release. In particular, greater use should be made of surface and microanalytical techniques to provide concentration profiles through the altered layer. It is recognized that the MCC intends to expand its leach testing experiments to include the effects of pH and Eh. However, we believe that thorough understanding of these effects will only be achieved in a specialized facility where, not only Eh and pH can be controlled, but also partial pressures of gases such as CO_2, flow rate, temperature and solution composition.

(d) It is believed that present solution analytical techniques are barely adequate to detect many elements dissolving from waste forms under high flow or long-term leaching conditions or for the leaching of materials of high durability. Alternatives to the present limited neutron activation procedures should be sought perhaps beginning with high performance liquid chromatography (HPLC).

(e) More consideration needs to be given to the interpretation of leach data of forms that can be used to demonstrate compliance with NRC release criteria. Although scale-up of leach rate data to a fractional release can, in principle, be calculated, for any size of monolith, experimental confirmation is still required so that the effects of surface imperfections and cracks can be included.

(f) A number of sampling difficulties are anticipated in the leach testing of monolithic waste forms. These will result from segregation due to slow cooling of the waste form. Thus, considerable attention must be directed to the size and shape of the final waste form so that any sample taken from it reflects the outer surface composition.

(g) Considerably more analytical development of surface area measurements for different waste forms is required. High confidence in these measurements is necessary for comparing the leaching rates of alternate waste forms such as glass and SYNROC.

(h) To date most mechanical testing of the waste form has centered on the quality assurance type of tests required to demonstrate stability during transportation accidents. By contrast, little attention has been given to evaluating various generic methods for the performance assessment of the waste form exposed to repository stress over geological time.

(i) Possible radiation effects on waste form leachability include internal alpha decay, ionizing radiation effects and internal transmutations. Tests under development, MCC-6 in particular, have the potential for developing the requisite information for licensing. However, the test requires qualification in several areas, particularly dose rate effects, temperature effects and radiation induced stresses.

(j) Internal doping is the recommended method for simulating internal alpha decay in waste forms, as opposed to external ion bombardment. However, it is essential that the damage mechanisms due to each method be understood. Comparative experiments using neutron and heavy particle bombardment may be useful for this purpose.

(k) The density and therefore the internal stesses of the waste form will be affected by ionizing radiation and internal alpha decay. This will be particularly important in multi-phase waste forms. Mechanical tests should be carried out in conjunction with irradiation to high dose levels.

8.2 Container Testing

(a) Corrosion studies of potential container materials, are as yet very inadequate for the requirement contemplated. This is particularly true for the more fundamental studies which will eventually be needed to demonstrate thousand year containment. No new tests specific to the long term integrity requirement have yet been generated.

(b) Electochemical corrosion studies hold some promise for use in testing for possible areas susceptible to pitting. Electrochemical experiments should, however be done in close coordination with other types of immersion tests. Underground redox conditions should be better understood, in conjunction with such studies.

(c) For the quantitative assessment of catastrophic failure of the container, a fracture mechanics approach is desirable, particularly when assessing the effects of stress corrosion and hydrogen embrittlement.

(d) Waste package design will be very important in determining corrosion. The use of backfill will markedly alter the chemistry of the groundwater. Thus backfills will have to be incorporated into tests at an early stage.

(e) Virtually no effort has been devoted to the standardization of generic methods for mechanical testing of container materials. Furthermore, stress conditions in repositories have received little attention.

(f) Many new techniques are available for non-destructive quality assurance tests. These include acoustic emission, eddy current inspection, radiography, dye-penetrant and helium leak detection, etc. The use of such techniques has apparantly not been contemplated for whole containers and should be investigated.

(g) For metallic containers, radiation can, for the most part, be viewed as an environmental variable in generic corrosion or mechanical testing procedures. It does not appear that unique analytic techniques will be required to evaluate the effects of radiation in container testing.

(h) Perhaps the most important effects of radiation on container corrosion in the repository environment will be associated with gamma radiolysis of corrosive media (or overpack/backfill/host rock material). Radiolysis effects on corrosion may be evaluated either by carrying out all corrosion tests under irradiation or by carrying out certain generic measurements to establish worst case conditions, and subsequently testing the material under these conditions. The latter method is most convenient, but research will be required to qualify the test procedure.

8.3 Backfill Testing

(a) Candidate backfill materials should be tested for their radionuclide retardation properties using dynamic systems such as column experiments. Using this approach, retardation factors and diffusion coefficients can be experimentally determined under realistic chemical, thermal, hydrologic and radiation conditions to obtain information for the comparative evaluation of backfill.

(b) The pore water chemistry of the radionuclide/backfill systems should be examined as a part of all tests. In cases where radionuclide breakthrough cannot be observed on a laboratory time scale, this information is absolutely necessary to determine the rate and extent of radionuclide migration. Where breakthrough can be observed such information can allow for the calculation of radionuclide partitioning between the solid and liquid phases and can also provide mechanistic data.

(c) The data obtained in terms of retardation factors and diffusion coefficients should ultimately be applied to mass-balance type models. These models can then be used to estimate radionuclide breakthrough times and release rates which can then be used to evaluate backfill performance in terms of the NRC criteria.

(d) Tests will be required to determine the effect of irradiation on backfill performance: these should include evaluation of external gamma irradiation effects, irradiation effects by sorbed nuclides on elution properties and gas generation from dry backfill.

8.4 Whole Package Testing

(a) Current designs for failed whole package are unrealistic and very limited data have been generated. The design of realistically failed components is desirable. In addition, combinations of components should be considered in support of whole package tests.

(b) With limited experimental data, the analytical assessment of waste package performance is inevitable. Comprehensive models are desirable which incorporate both the experimental data and probabilistic descriptions.

APPENDIX A

LETTER REPORT ON APPLICABILITY AND LIMITATIONS OF CORROSION DATA FOR PREDICTING LONG TERM CONTAINMENT

M. S. Davis and D. G. Schweitzer

ABSTRACT

Theoretical justification for predicting long term corrosion rates from shorter term experiments requires that the mechanism of corrosion remain constant over the time required for the prediction. Furthermore, the mechanism must be experimentally validated by the determination of an explicit, isothermal rate expression which accounts for the correct functional dependence of the corrosion process on all the parameters involved in corrosion. We are not aware of any such evidence for those metals being considered for use in a high level waste package.

Thermal and isothermal methods of accelerating the corrosion rate are considered. We note reasons why the use of elevated temperatures to increase corrosion rates for the purpose of predicting long term corrosion at the lower temperature are theoretically unjustified and technically unsound.

Although isothermal acceleration techniques such as increasing the concentrations of reactants are useful in homogeneous kinetics, we do not believe they have been rigorously justified for heterogeneous corrosion reactions.

Possible methods of achieving approximately 1000-year containment through design concepts rather than metal component corrosion resistance are discussed.

INTRODUCTION

This report addresses the applicability and limitations of short term laboratory tests intended to predict the long term (approximately 1000 year) corrosion behavior of metals considered for use in disposal of high level waste. These comments are based on our evaluation of the data reviewed in Tasks 1, 2, 4 and 5 of the BNL waste package program. It is our contention that no metal being considered for use in a high level waste package has yet been studied in enough detail to justify a prediction of its long term corrosion behavior.

ISOTHERMAL PREDICTIONS

Corrosion is a kinetic, non-equilibrium process. The rates and mechanisms of corrosion are dependent upon, among other parameters, the reactants and products of the various corrosion processes.

In order to predict the corrosion rate for times appreciably longer than those studied, the mechanisms of corrosion must be accurately known and it must be assumed that they remain the same over the time required. One of the major obstacles in determining corrosion mechanisms results from observations that rates of corrosion can be seriously altered by the corrosion products and how they are distributed or removed from the corroding interfaces. (Corrosion products can cause either catalysis or inhibition.)

In general, there are more requirements for heterogeneous systems than for homogeneous systems on the use of isothermal rates to predict for times much longer than the time over which the rates were measured. Homogeneous kinetic systems tend toward equilibrium states that are usually well defined. If the isothermal rate expression is rigorously correct and truly represents the mechanisms of the reaction, it will include all the chemical, physical and geometric factors that are known to alter the rate. For homogeneous systems this can be tested by using the known equilibrium values and showing that the rate goes to zero.

This test is generally not feasible for complicated heterogeneous reactions such as solids corroding in liquids. Here too, it is mandatory in determining the mechanism to show that the isothermal rate expression includes the correct functional dependence of the corrosion rate on all the chemical and physical variables known to affect the rate of corrosion. For heterogeneous reactions, however, it is also necessary to prove that neither the metal nor the metal-solution interface undergoes any structural, physical, or chemical change that can alter the corrosion rate over the total time for which the prediction is intended.

For metals such changes might include:

- isothermal stress annealing in the bulk
- formation and subsequent breakaway of a surface film
- stresses developed or removed by formation or cracking of a corrosion product or film
- diffusion of corrosion products into or out of the metal surface
- diffusion of bulk components into surface depleted zones
- initial selective attack at a site that eventually is depleted
- grain size changes
- grain boundary precipitation, etc.

Any or all of these might lead to a change in the corrosion rate with time. In general, the overall corrosion rate of most metals represents contributions from several different mechanisms with different temperature dependencies. These can interact with each other sequentially. For example, consider a corrosion process where an oxide layer is formed by one component in an alloy,

eventually builds up, spalls, and continues to form depleting the zone beneath the surface. Over periods of time long compared to the time necessary to form the film, the component will diffuse from the bulk to the surface depleted zone. If this component is in equilibrium with its own carbide for example, depletion of the bulk concentration by formation of a surface oxide will eventually cause the carbide to decompose increasing the carbon activity of the alloy. This, in turn, could lead to formation of a new carbide with a different component of the alloy so that short term corrosion rates will not represent the corrosion rates that would occur over longer times. Even in the case of uniform corrosion, Uhlig has noted[1] "it is often not safe to extrapolate a reported rate to times of exposure far exceeding the test period."

Altering concentrations of reactants and products to test if a single rate expression accounts for the observed corrosion behavior may be more significant for uniform corrosion than for pitting corrosion. Nevertheless, it is, even for uniform corrosion, a necessary but not sufficient condition for justifying time predictions.

In the cases of pitting corrosion, the basic properties of the pitting phenomena indicate that several mechanisms operate simultaneously. For a single mechanism, pits should occur uniformly in space, proceed with the same depth dependence on time, and develop the same shapes.

In real systems, pitting generally occurs at structural irregularities or chemical inhomogeneities that vary from sample to sample. Measurements within the pits, of solution compositions and corrosion product concentrations, show that each pit can be a different chemical system with different mechanisms operating at different times. This is also supported by the wide variability in induction periods, the variability in rates of penetration, and the variabilities in shape development and pit morphology.

For corrosion data in such systems to be meaningful, some type of statistical description of the pitting behavior has to be given. The quality of the statistical description with respect to its ability to predict long term corrosion behavior will be dependent on the quantity and precision of the experimental data. We note as an illustration of some of the problems associated with describing specific pitting corrosion, a discussion from a recent report on a Westinghouse conceptual design for a waste package (AESD-TME-3087 Draft, March 1981).

"Pitting can have its inception in a microscopic surface chemical inhomogeneity, in a physical irregularity, or even in a statistical fluctuation in local corrosion rate. If incipient conditions stabilize sufficiently, pit formation occurs; rapid dissolution occurs within the pit while the cathodic reaction occurs outside it, on adjacent surfaces. The process is autocatalytic, tending to produce an excess of positive charge within the pit, which attracts negatively charged chloride ions (the less mobile OH^- ions remain outside the pit and participate in the cathodic reaction); these further stimulate metal dissolution and create more positive charge. The hydrolysis of excess $FeCl_2$ accumulating within the pit produces excess hydrogen ions, and the pH decreases (pH values as low as two have been measured in pits occurring

in basic bulk solution environments); this further stimulates dissolution. At the pit/solution interface, insoluble corrosion products tend to form due to a reaction between the OH^- ions outside the pit and the ferrous ions within it.

Pit growth can be impeded by the resistance thus interposed to the migration of ions, or it can be impeded by the pit's own depth and low aspect ratio, which also reduces the rate of ionic migration. Thus, a pit can stop growing if choked with its own debris. However, in a solution which is sufficiently aggressive, so many pits may form that they tend to coalesce. When this occurs, the effect is that of general corrosion, advancing, however, at the higher rate associated with pit formation.

The solution within a pit tends to be concentrated, and therefore more dense than the bulk solution. Accordingly, gravity has an effect, so that lateral and especially inverted pits tend to cease growth quickly, as the denser solution drains out. On the other hand, lateral pits can turn downward from gravitational influence and can form long channels underneath and parallel to a vertical surface. Further general corrosion will then expose such undercut grooves, and the groove surfaces can be sites for further pits. Top surfaces, of course, represent the worst pitting sites, because the gravity effect tends to stabilize pit growth and pit progress is exactly in the direction for maximum depth of penetration."

Stressing that the most valid justification for predicting long term corrosion rates is the existence of an explicit, highly precise isothermal reaction rate which includes the correct functional description of the corrosion rate on all possible parameters involved in corrosion, we believe that there is as yet no such evidence for any metal being considered for use in a high level waste package.

TEMPERATURE ACCELERATION

It is our view that the use of elevated temperatures to increase corrosion rates for the purpose of predicting long term corrosion behavior at the lower temperature can be theoretically unjustified and technically unsound. The effects of changing temperatures in chemical kinetics are covered by Arrhenius' concepts and theories. These concepts are valid only if it is assumed that the same mechanism occurs over the temperature range studied. If this assumption happens to hold, the ratio of the rates at different temperatures can be used to obtain the numerical value of a constant called the activation energy. This numerical value can then be used to speculate on what processes are involved in delaying the reactants from forming the thermodynamically more stable products instantaneously.

If several rate measurements are made at several temperatures and if they are precise enough to demonstrate a single numerical value for the activation energy, this type of result can be used to claim that the data are consistent with the assumption that the mechanism did not change over the temperature range.

Rigorously, however, these measurements do not prove the existence of a single mechanism. Thermal barriers (activation energies) for different mechanisms can have similar values. An additional necessary test to verify a constant mechanism is to demonstrate that the individual rate constants at all temperatures are identical in functional form with respect to all the variables involved in the corrosion process. This requirement implies that temperature acceleration is subject to all the problems and uncertainties of isothermal prediction techniques in addition to many complications that can be introduced by the temperature variation itself. It should be clear that a temperature change that causes a phase change in any reactant (i.e., water going to steam) has the potential to drastically alter the corrosion process. Recalling, that if the overall corrosion rate is the result of several mechanisms with different activation energies, changing the temperature, in principal, will change the mechanism and will invalidate any use of the high temperature rate in predicting long term behavior of the low temperature corrosion process.

In summary, we believe (1) that existing isothermal corrosion data are inadequate for demonstrating long term integrity for any metallic component being considered for a high level waste package and (2) that the use of temperature accelerated corrosion rates to estimate long term corrosion at lower temperatures is, by itself, unacceptable for assuring long term integrity for metallic components of the waste package.

CONCLUSIONS

Although corrosion data on individual metallic components are at present inadequate to satisfy regulatory criteria for long term containment of high level waste, we believe such containment can be achieved through any of several design concepts which utilize either

- isolation of the waste package from the corroding environment
- sacrificial materials which consume or deplete the corroding agents
- materials which significantly inhibit the corrosion rates
- combinations of the above, such as canisters within canisters separated by annular volumes filled with absorbers, ion exchange media, graphites, zeolites, etc.

REFERENCE

1. Herbert H. Uhlig, Corrosion and Corrosion Control, 2nd Ed., John Wiley and Sons, New York, New York, 1963, p. 13.

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16. ABSTRACT (200 words or less)

This report reviews DOE's development of methods for testing high-level nuclear waste packages. These methods are for potential use in comparative tests of alternative materials and components, in tests designed to control the quality of the materials used in the waste package and eventually in tests to demonstrate that the waste package will meet the proposed regulation for disposal of high-level nuclear waste (proposed 10CFR60).

This review includes the activities of the Materials Characterization Organization. This organization is dealing successfully with comparative testing but, in general, has not yet addressed compliance testing.

Testing and characterization of each component are discussed in separate chapters. Testing of the waste form is considered in terms of chemically induced changes (leaching), mechanical effects and radiation effects. Waste container testing involves corrosion investigations, mechanical testing and studies of radiation effects. Testing of geologic backfill is discussed with the emphasis placed on the ability of the backfill to retain radionuclides under different aqueous flow conditions. Finally, the differenc objectives for whole package testing are reviewed and compared to recent experiments started in DOE laboratories. Recommendations for further research are made and general types of compliance tests are identified.

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